The Photochemistry of Five-membered Nitrogen-Heterocycled(Dissertation_全文)

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THE PHOTOCHEMISTRY OF FIVE-MEMBERED NITROGEN-HETEROCYCLES

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1975

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P E R F A C E

The studies included in the present thesis have been carried out under the guidance of Professor Teruo Matsuura at Kyoto University during 1970-1974. The studies are concerned with the photochemical reactions of five-membered dihydroheteroaromatics and of donor-acceptor systems including imidazoles as the donor.

I am greatly indebted to Professor Teruo Matsuura for his assistance in directing and encouraging this work. My greatful thanks are also made to Dr. Isao Saito for his helpful advices and discussions. Furthermore, my greatful thanks are made to Dr. Akira Nishinaga, Dr. Ruka Nakashima and all the members of the research group of Professor Teruo Matsuura.

Finally, I would like to thank my wife for typing this thesis.

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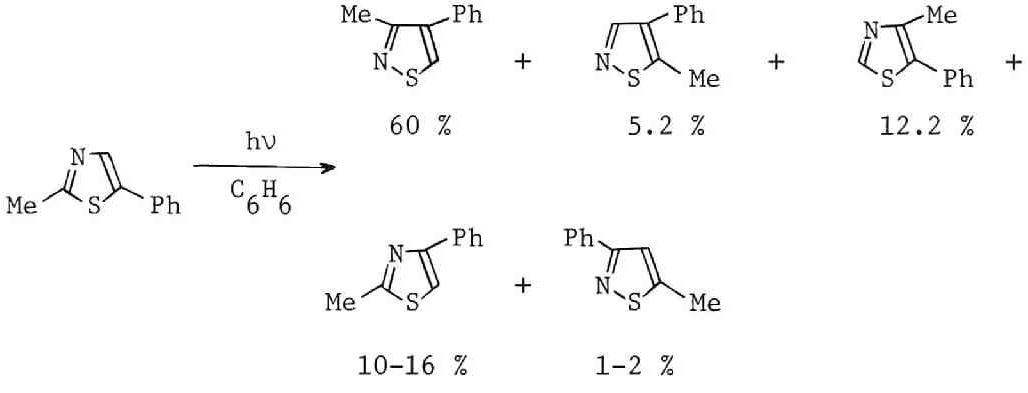
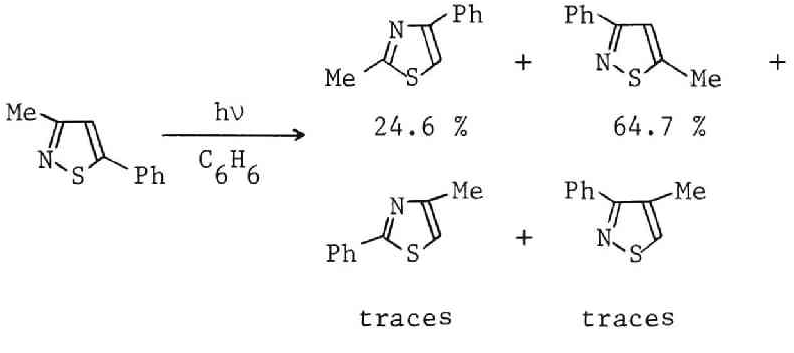
C O N T E N T S

G E N E R A L I N T R O D U C T I O N

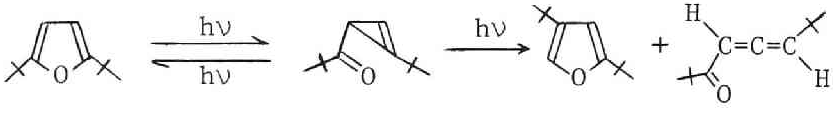
Five-membered heteroaromatic compounds have received much attention in organic photochemistry.[1] On absorption of UV light, these compounds undergo various reactions, such as rearrangement, fragmentation, addition and substitution. Since the first irradiation-induced conversion of a benzenoid to a valence bond isomer of Dewar benzene-type was reported in 1962,[2] a number of interesting and apparently related rearrangements, that is, valence isomerization and transposition of ring atoms have been reported for five-membered heterocycles. For example, thiazoles and isothiazoles[3] undergo a complex





transposition of ring atoms. Many other heterocycles, such as furans, thiophenes, isoxazoles, pyrazoles and so on, undergo similar transposition reactions. In general, the course of these photochemical rearrangements has been interpreted either by three-membered ring intermediates(A), by the intermediacy of Dewar structures(B), by an equilibrium between A and B,[5] by the Kellogg mechanism,[4] or in the case of sulfur-containing heterocycles by the intermediacy of zwitterionic species(C, D). In some cases, such intermediates were isolated as shown below. However, in many cases, the exact pathways of the

(A)



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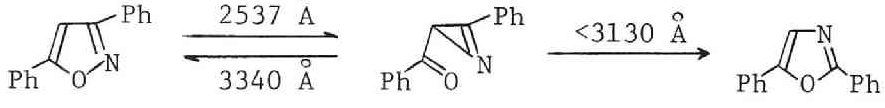

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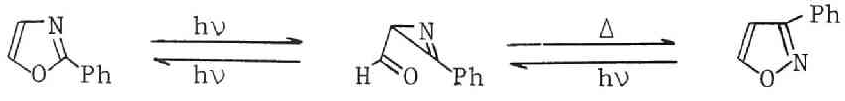

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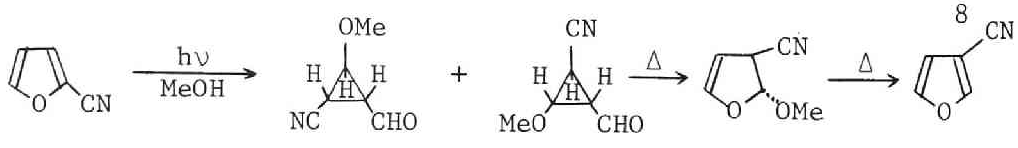
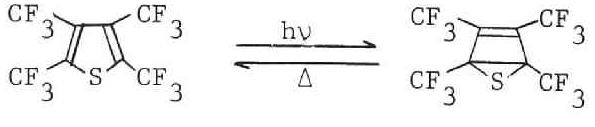


(B)



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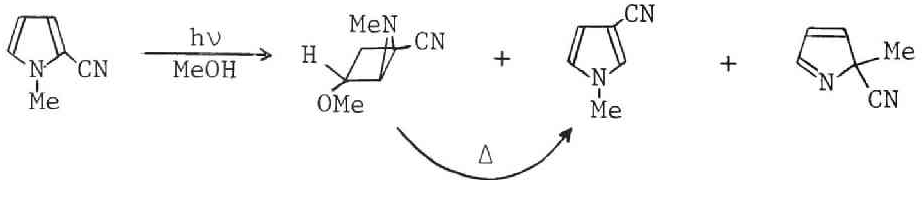

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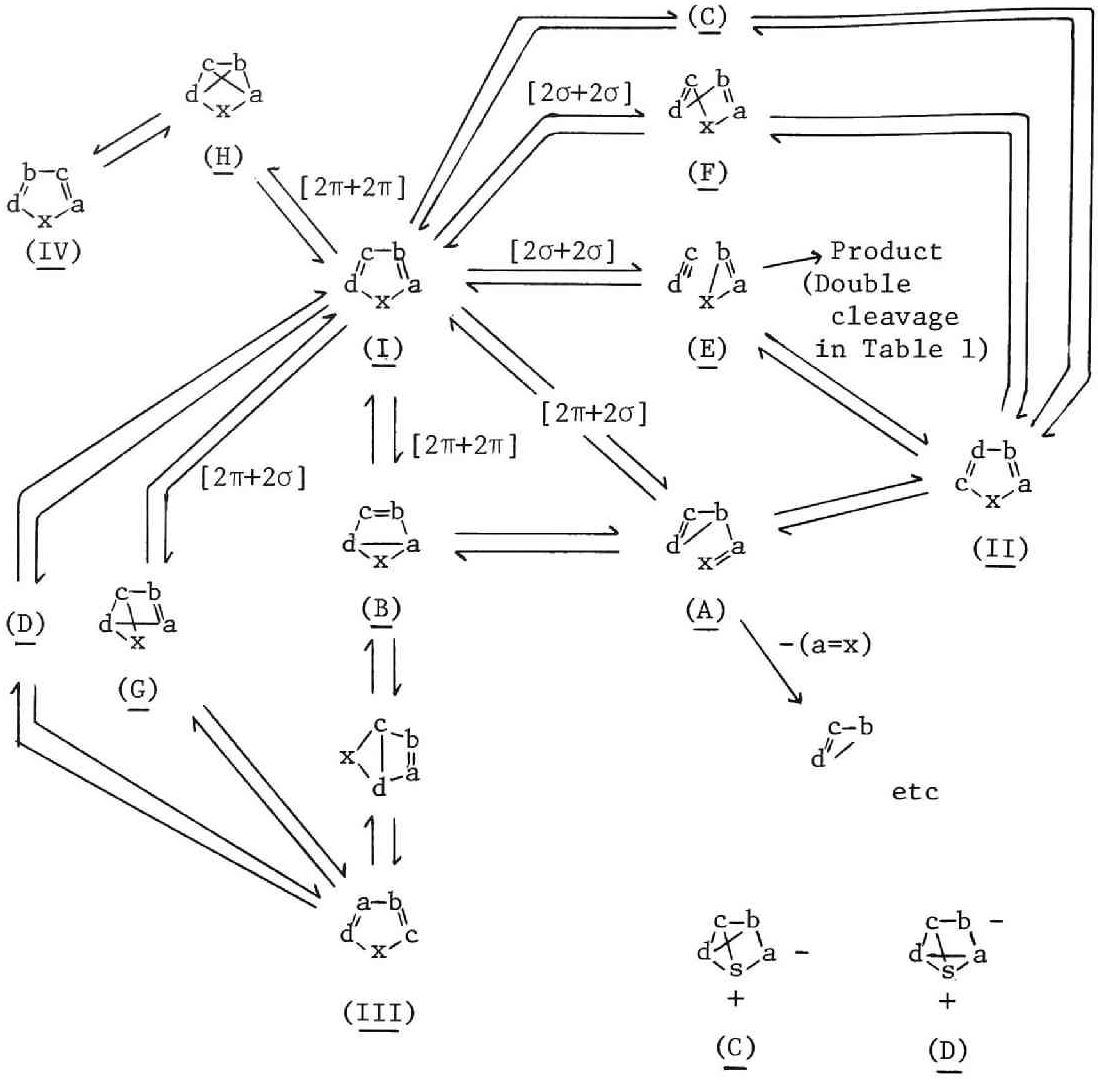
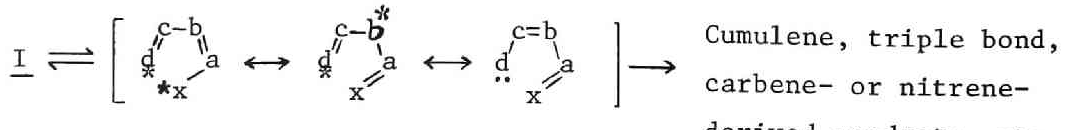
reactions remain unknown.

Scheme 1 describes the general mechanism for rearrangements and fragmentations of five-membered aromatic heterocycles represented as formula I. Most of these reactions are formally regarded as a sequence of [2 + 2] reactions. The bond crossing [2 + 2] reactions leading to F, G and H are equivalent to the Kellogg mechanism, if they are regarded simply as geometrical distortion of the ring in excited states. Double cleavage, which is a [2 + 2] reaction to divide a molecule into two, E and c≡d, is observed frequently in heteroaromatics containing three or more heteroatoms.[1] Since E is usually equivalent to a 1,3-diradical or a 1,3-dipolar species, it is led to stable final products through some steps. In cases of furan, thiophene and pyrrole, elimination of the a=X fragment from A was frequently observed in vapor phase.[11] If cleavage of the weakest ring bond is supposed to occur before [2 + 2] bond formation, cumulene,[12] triple bond,[13] carbene (nitrene)-derived products,[14] etc.[15] can arise thereof. As a matter of fact, Scheme 1 can explain many rearrangements and fragmentations of heterocycles and these reactions are classified as shown in Table 1.

In transposition reactions, all of A, C and F can simply effect the interchange of adjacent atoms(or groups) a~b or c~d, if an equilibrium between A and B is not considered. Thus, reactions leading to II via A, C and F are classified as Group I. In a similar way, reactions leading to III via B, D,and G are classified as Group II, in which the products do not change the order of array of atoms (or groups), a, b, c and d on their rings. In cases where sufficient evidence was

Scheme 1. Possible pathways for rearrangements and fragmentations of five-membered aromatic heterocycles (I)





x= O, S or NR
a, b, c or d= C or N
*= • or +, -

Table 1. Classification of rearrangements and fragmentations of five-membered aromatic heterocycles.

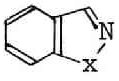
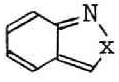
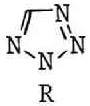
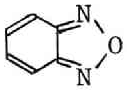
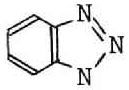
Heteroaromatics		Type of Transposition[a]				Type of other reactions[b]		
		Group I	Group II	Group III	E	Double cleavage	Single cleavage	-(a=x)
	x=O	o(A)					o	o
	S	o	o	o				o
	NR		o(B)					o
	x=O	o(A)[c]					o	
	S	o	o	o				
	NR	o	o					
	x=O	o(A)	o					
	S	o	o	o				
	NR		o					
	x=O	o[c]					o	
	S						o	
	NR						o[d]	
	x=O		o				o	
	NR		o				o	
	x=O				o	o		
	S					o		
	NR					o		
	x=O						o	
	x=S		x=S					
	NR		NR			o		
 R		 R						

Table 1. (continued)

a) See Text.

Group I - a, b-interchange type

Group II a, b, c, d-fixed order type

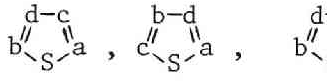
Group III --- other transposition

E --- transposition via double cleavage

b) See Scheme 1.

c) cf. J. P. Ferris, F. R. Antonucci and R. W. Trimmer, J. Amer. Chem. Soc., 95, 919 (1973) ; 96, 2014 (1974). L. J. Darlage, T. H. Kinstle and C. L. McIntosh, J. Org. Chem., 36, 1088 (1971).

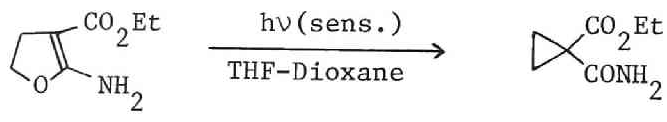
d) It is proposed that N-unsubstituted indazoles rearrange via 2H-indazoles to benzimidazoles [H. Tiefenthaler, W. Dörscheln, H. Göth and H. Schmid, Helv. Chim. Acta, 50, 2244 (1967)].

provided for the intermediate of reaction, the type of intermediate is shown in parentheses. Although E should belong to Group I, it is placed on another column, because a transposition via such a double cleavage seems easily distinguished from that via A, C and F by examining side-reactions. Of course, C and D are excluded, when a heterocycle does not contain sulfur. In cases of thiophenes,[16] thiazoles[3] and isothiazoles,[3] other types of transposition, such as the interchange of c and d and the scrambling of a, b, c and d like  , etc., also take place (Group III). In order to explain such complex rearrangements, an equilbrium between A and B or the Kellogg mechanism must be taken into consideration.

Although, to say nothing of the type of rearrangements, there exists no rule always strictly adhered to to predict the direction of rearrangements, it can be said that major products arise from cleavage of the weakest single bond in the lowest excited states[17,18] and via intermediates (A and B) stabilized by, for example, phenyl conjugation.[3,5]

In contrast to a vast and fascinating study concerned with the photochemistry of aromatic heterocycles, the photochemical behavior of only a narrow variety of dihydroheteroaromatics had been studied in detail. The author undertook an investigation on the photochemistry of five-membered dihydroheteroaromatics such as Δ^2-thiazolines, Δ^2-imidazolines, Δ^2-isoxazolines, Δ^2-oxazolines, Δ^3-oxazolines,etc., which will be detailed in this thesis. An extensive account of the results

obtained by other workers is outside the scope of this chapter, but following examples may be rather enough to understand reactions so far found. From these example-s, coupled with the author's results (Part I, Chapter I-III), it can be seen that dihydroheteroaromatics have a striking analogy with heteroaromatics in that formal intramolecular [2 + 2] reaction between ring bonds frequently occurs. Furthermore,



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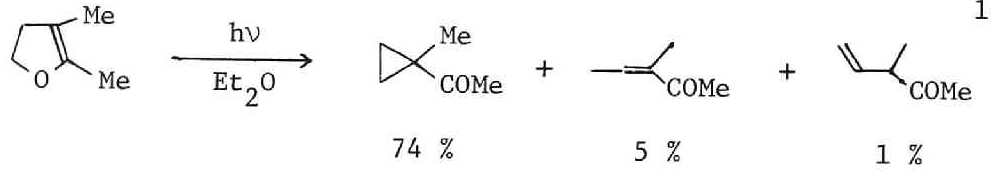

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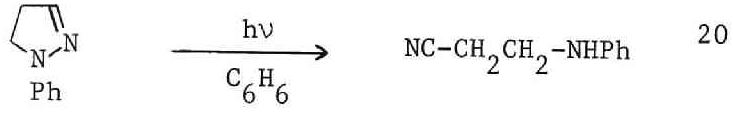

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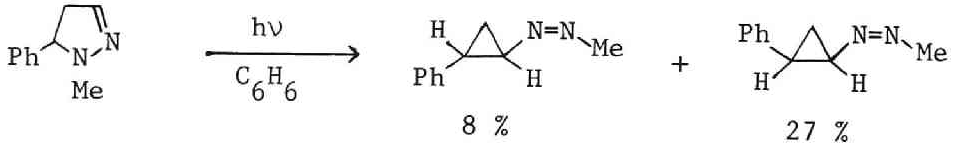

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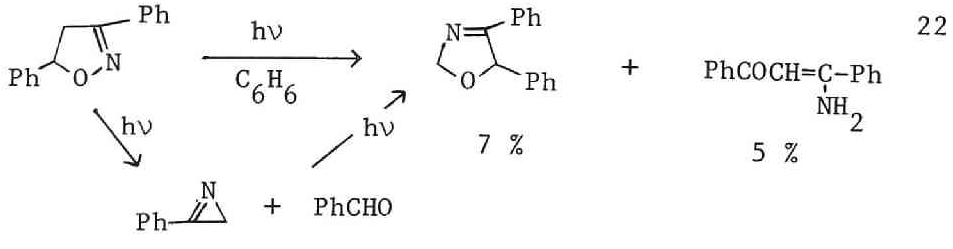

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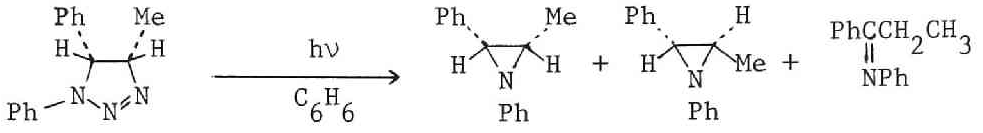

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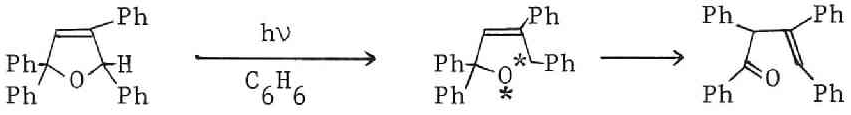

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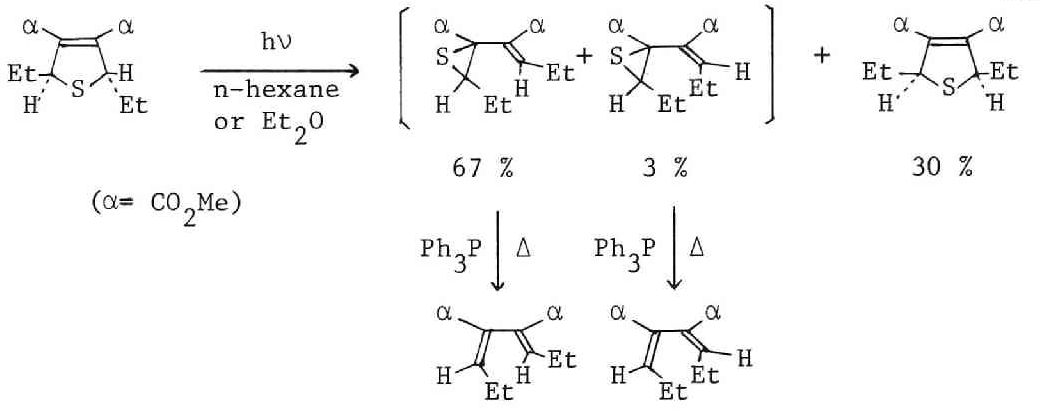

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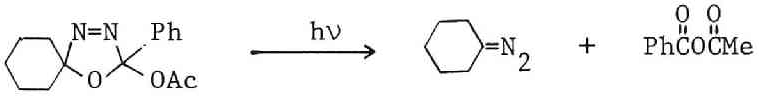

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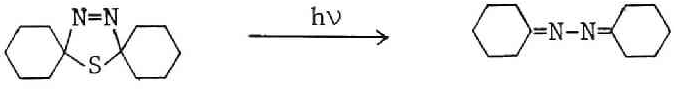

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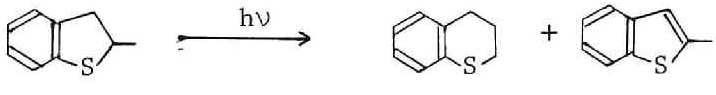

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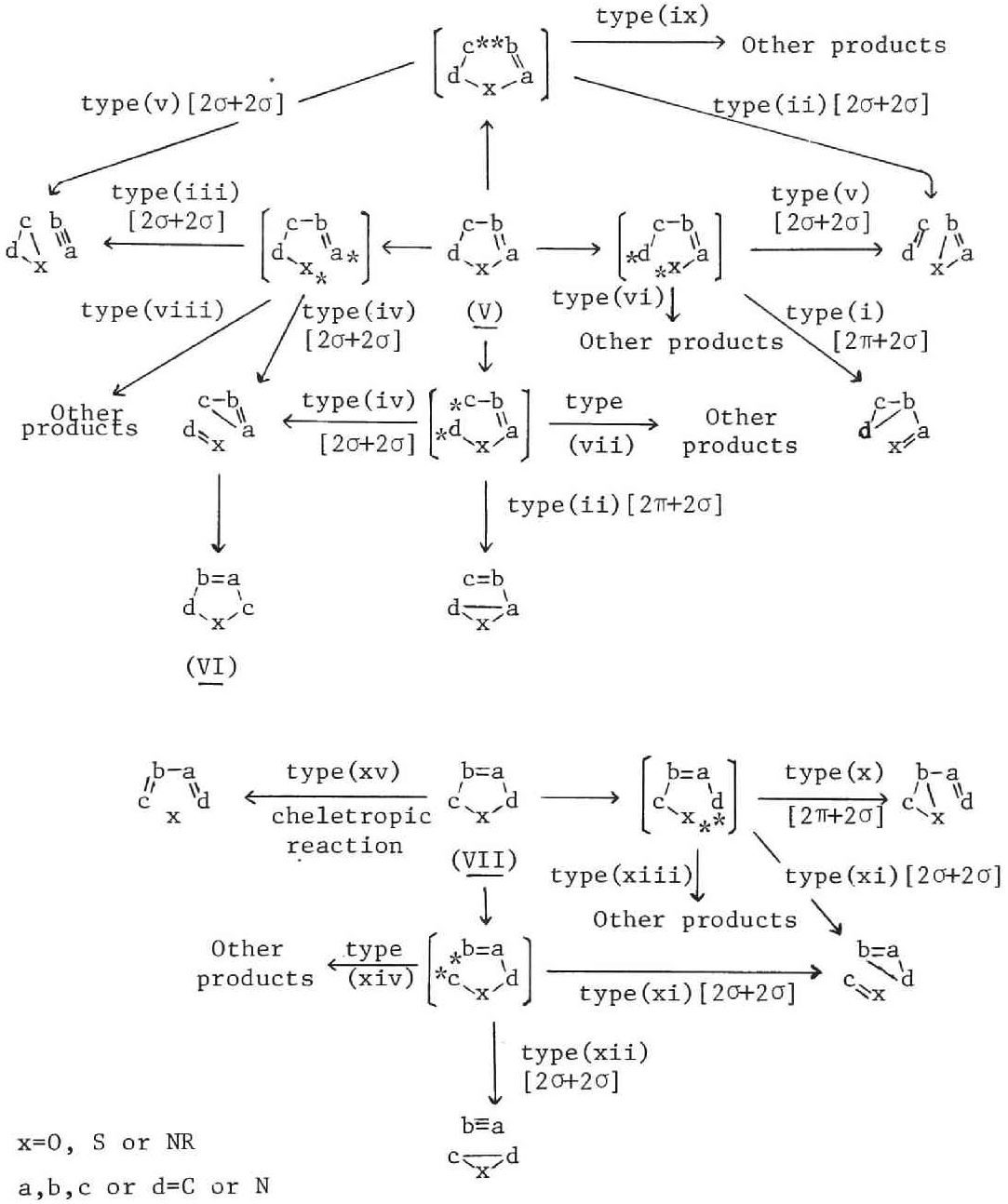
side reactions (often main reactions) which are initiated by breakage of a weak ring bond and result in, for example, the migration of hydrogen atom or phenyl group also frequently take place in both systems. Terefore, a general scheme analogous to Scheme 1 can be drawn for the classification of photoreactions of dihydroaromatics (Scheme 2). Three-membered cyclic intermediates resulting from these [2 + 2] reactions cannot always be isolated, but in many cases they undergo further photochemical or thermal transformation into the final products.

It has been suggested that the formation of a cyclopropane ring or its hetero-analog from 4,5-dihydrofurans,[19,29,30] Δ^2-pyrazolines,[30] Δ^2-thiazolines (Chapter I) and 2,5-dihydrothiophenes[25] may involve a concerted nature. Some experimental results with Δ^2-isoxazolines (Chapter II) also argue for partial concertedness of certain [2 + 2] reactions. The dichotomous thermal and photochemical reactions of Δ^3-1,3,4-thiadiazolines and Δ^3-1,3,4-oxadiazolines are also well explained by a concerted mechanism.[25] Therefore, some of the [2 + 2] reactions of dihydroheteroaromatic might exactly resemble the valence bond isomerization of heteroaromatics.

In principle, various types of transposition of the ring atoms of dihydroheteroaromatics will be possible by proceeding through a sequence of [2 + 2] reactions. For example, it is expected that dihydroheteroaromatics(V) are transformed into dihydroaromatics(VI) via [2 + 2] reaction of type(iv) followed by further [2 + 2] reaction (Scheme 2). A transposition reaction of this type was actual-

Scheme 2. Possible reaction pathways of five-membered dihydroheteroaromatics (V and VII).



x=O, S or NR

a,b,c or d=C or N

*=•, + or -

Other products=generally, isomerization products

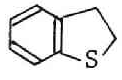
ly observed by Schmid and independently by the author in the case of Δ^2-isoxazolines. Other types of transposition will be found in the near future. Since a number of three-membered ring compounds resulting from [2 + 2] reactions of dihydroheteroaromatics are potentially 1,3-dipolar species, the exchange of atoms in a five-membered ring will be able to be caused by using in situ appropriate dipolarophiles (see Part I, Chapter II).

Besides the above reactions, five-membered dihydroheteroaromatics undergo frequently photoaromatization in the presence or absence of a photochemically generated hydrogen abstractor to the corresponding aromatics (Part I, Chapter IV and V). In Table 2, the author compiles, to his best knowledge, all of the known types of reactions of the excited states of alkyl- and aryl- substituted five-membered dihydroheteroaromatics.

Among the pathways shown in Scheme 2, the pathway that the weakest ring bond is broken or more stable molecules are produced appears predominant as a rule, although the reaction of 2,3,5,5-tetraphenyl-2,5-dihydrofuran is initiated by cleavage of the stronger bond in the molecule.[24]

The photochemical behaviors of structurally similar noncyclic analogs of dihydroheteroaromatics has been scarcely studied. Some of the examples are shown below. The third example may be regarded as a bond-crossing [2 + 2] reaction, which is not observed in Δ^2-isoxazoline systems (Part I, Chapter II). In the first and the second examples, no [2 + 2] reactions were observed, while cyclic analogs,

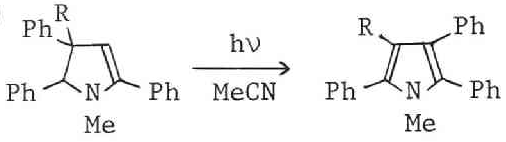
Table 2. Types of reactions of excited states of five-membered alkyl- and aryl-substituted dihydroheteroaromatics.

Type (A) Compounds		Types of Reaction							
		[2 + 2] reaction				single cleavage			others
		type (i)	type (v)	type (iv)	type (iii)	type (vi)	type (vii)	type (viii)	
	x=O	o				o			
	NR								a, b
	PR								c
	x=O		o	o	o			o	
	NR	o						o	a, d
	x=O[e]			o			o		
	S	o			o				
	NR			o			o		
					o				
						o			a

Type (B) Compounds		type (x)	type (xi)	type (xii)	type (xv)	type (xiii)	others
	x=O		o[f]			o	
	S	o				o	a
			o				d
	x=O		o	o			
	S				o		

Table 2. (continued)

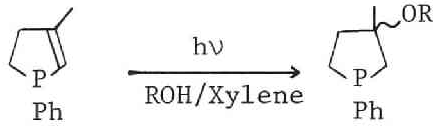
a) Photoaromatization (See Chapter IV of Part I).

b) 

R=Ph ca. 15 %

R=Me 23 %

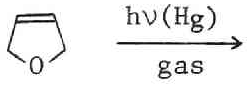
[Unpublished data]

c) 

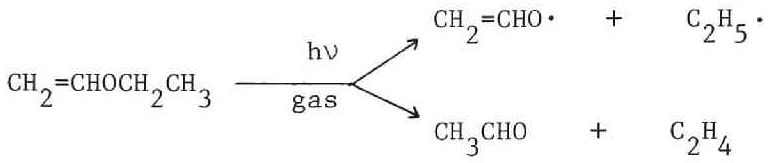
[H. Tomioka and Y. Izawa, Tetrahedron Letters, 5059 (1973)]

d) 1,3-shift of ring hydrogen (See Chapter II of Part I).

e) See Chapter III of Part I.

f)  $\xrightarrow[\text{gas}]{h\nu(Hg)}$ CO + $CH_3CH{=}CH_2$ + H_2 etc

[B. Francis and A. G. Sherwood, Canad. J. Chem., 48, 25 (1970)]



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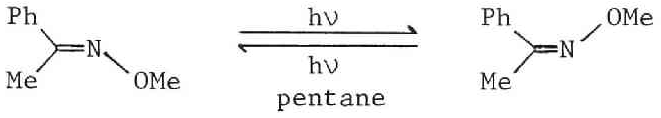

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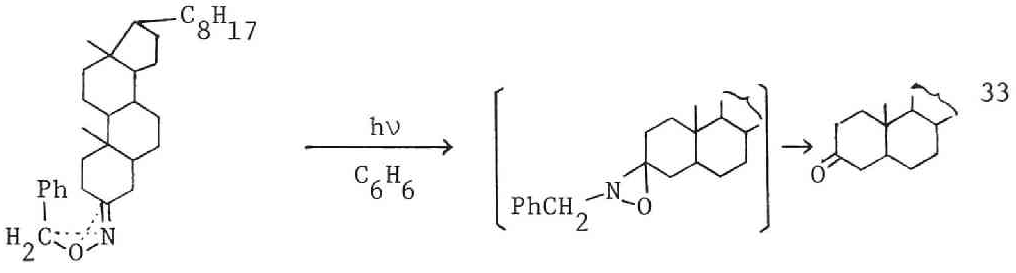

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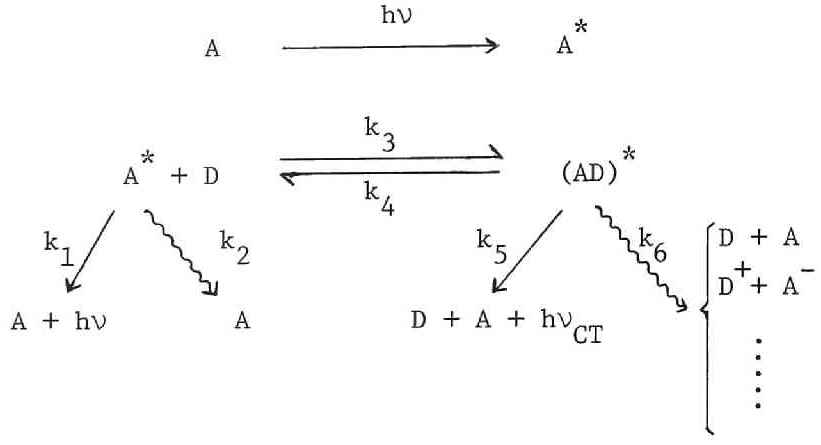
4,5-dihydrofurans and Δ^2-isoxazolines, undergo [2 + 2] reactions.

In general, an electronically excited molecule relaxes by emission, internal conversion and intersystem-crossing. In a weak donor(D)-acceptor(A) system which does not form a complex in the ground state, however, formation of an exciplex is an important mode of deactivation. These processes are schematically represented by Scheme 3 where the asterisks, solid arrows, wavy arrows, $h\nu_{CT}$ and k designate excited electronic states, radiative pathways, nonradiative pathways, exciplex emission and rate constants, respectively. It is of particular importance that an ion radical pair can be formed, possibly via an exciplex,in polar solvents. Exciplex fluorescence and the ionic dissociation of exciplexes have been studied in detail for aromatic hydrocarbon-amine systems.[34] Fluorescence quenching

Scheme 3



studies for aromatic hydrocarbon-diene systems have been also extensively done.[35] Besides the above pathways in Scheme 3 exciplexes can relax by chemical reaction. Photochemical reactions (usually photoaddition) which are interpreted as occurring via exciplexes and radical ions have been found for many donor - acceptor systems such as aromatic hydrocarbon-amine,[36] aromatic hydrocarbon-diene,[37] aromatic hydrocarbon-cyano compound,[38] carbonyl compound-amine,[39] and aromatic nitrile-olefin[40] systems.

As outlined above phenomena involving formation and reaction of exciplexes have been the subject of much recent investigation. The author has studied the photochemistry of an imidazole-acrylonitrile system (Part II, Chapter I and II), and found that its photochemical reaction is interesting in view of current interests in the fate of exciplexes in a variety of polarity of solvents. The author pays attention to the biological importance of imidazoles as a moiety of purines which are one of molecules whose charge-transfer complexes

are considered to play a part in the mechanism of biochemical reactions.[41] In chapter III of Part II novel photoreactions of an imidazole-2-cyanopyridine system, namely, photocycloaddition of the cyano group and dimerization sensitized through an electron transfer, will be described.

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P A R T I

C H A P T E R I

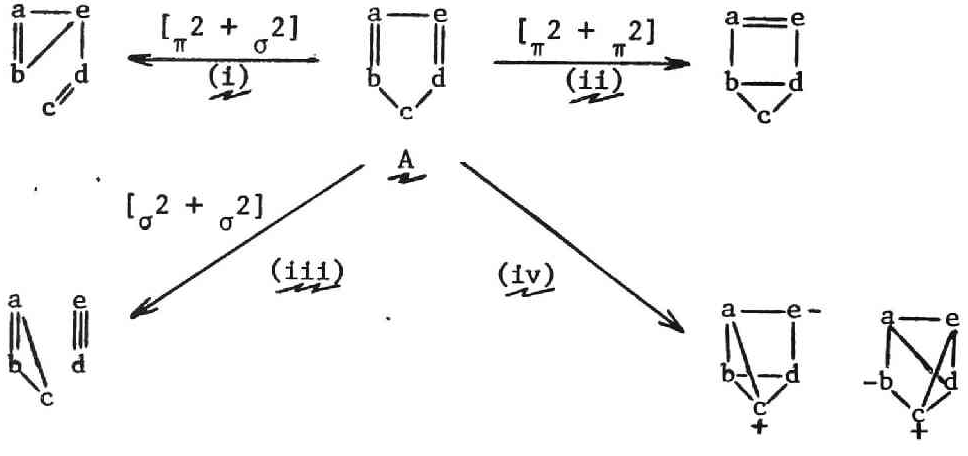
The Photochemistry of 2-Thiazolines

Upon irradiation with light at 2537 Å 2-alkyl-2-thiazolines(I) underwent rearrangement to N-alkenylthioamides(II and III) as the major pathway and fragmentation to a nitrile and an episulphide as the minor one. Evidences are provided for the intermediary formation of a valence bond isomer, N-thioacylaziridine, followed by its photochemical transformation into N-alkenylthioamides.

1. Introduction

The photochemical reactions of five-membered heteroaromatics have attracted attention of many workers.[1] Among them, the photochemical rearrangement and fragmentation reactions of type A compounds (c=O, S, or NR) have been interpreted mostly in terms of one of three types of valence bond tautomerization formally regarded as [2 + 2] reactions (i, ii, and iii in Scheme 1),[1,2] although in particular cases (c=S) some evidences have been provided for the occurrence of type iv of valence tautomerization.[1,3]

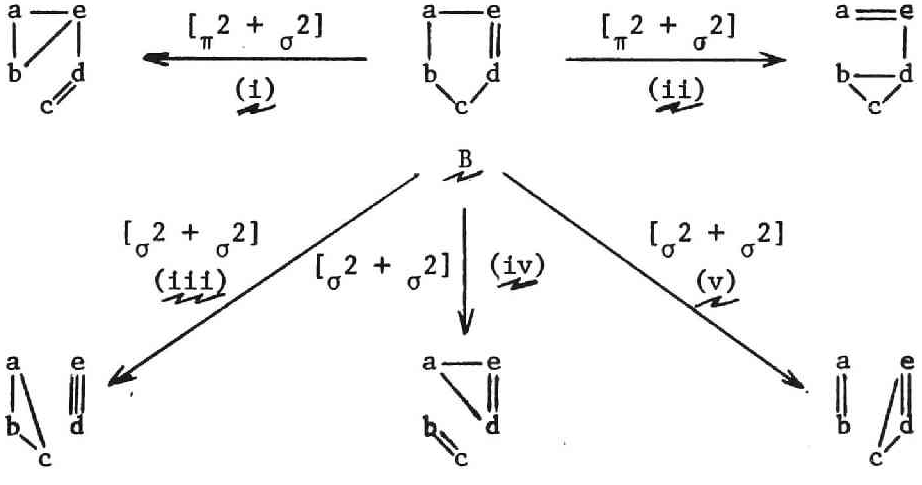
Scheme 1



On the other hand, there have been fewer reports on the photochemical reactions of partially hydrogenated five-membered heteroaromatics of type B (c=O, S, or NR). By analogy with the photochemical [2 + 2] reactions of Scheme 1, type B compounds would be expected to undergo

the following five types of photochemical [2 + 2] reactions (i-v in Scheme 2). It has already been known that reaction i occurs with 4,5-dihydrofurans,[4] 2-pyrazolines,[5] and 2-thiazolines,[8] reaction iii with 2-thiazolines,[8] 1,2,3-triazolines,[6] and 2-isoxazolines,[7a] reaction iv with 2-isoxazolines,[7] and reaction v with 2-isoxazolines.[7a,#] However, three-membered cyclic compounds resulting from such reactions cannot always be isolated, but in many cases they undergo further photochemical or thermal transformation into the final products. An exceptional case is found in the photochemical rearrangement of 4,5-dihydrofurans which give acylcyclopropanes.[4] In the present chapter the author will

Scheme 2



The photochemical valence tautomerization of dihydroheteroaromatics of type B (b=hetero atom) has also been known.[9]

describe the studies of the photochemical reactions of 2-thiazolines involving reactions i and iii in full detail, and the photochemistry of 2-isoxazolines will be presented in the next chapter. (Hereafter the designation, reaction i, ii, etc. will be used for the pathways in Scheme 2.)

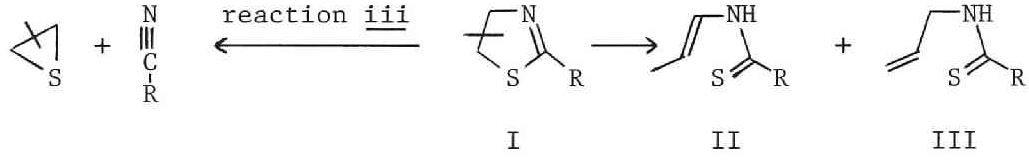
2. Results and Discussion

Photolysis products of substituted 2-thiazolines.

Several 2-alkyl-2-thiazolines Ia-Ig were irradiated in acetonitrile with light from a low-pressure mercury lamp with Vycor housing (mainly 2537 Å). In most runs, after evaporation of the solvent the residue was found by NMR analysis to consist mainly of the starting material and its rearranged products, N-alkenylthioamides II or/and III. In the case of Ic it contained additionally benzyl cyanide. These products were isolated by silica gel chromatography and their structures were determined on the basis of the chemical and spectral evidences or by direct comparison with authentic samples (see Experimental). Among these products, N-vinylthioacetamide(II a) was unstable to heat (above 80°) to decompose, but considerably stable under similar irradiation conditions to give only a small amount of polymeric product. The conditions and results of the photolysis experiments are presented in Table 1.

In some cases, attempts were made for searching of products other

than II and III. Thus, ethylene sulfide was obtained from 2-methyl-2-thiazoline(Ia), propionitrile from 2-ethyl-2-thiazoline(Ib), and benzyl cyanide from 2-benzyl-2-thiazoline(Ic). The results indicate that 2-alkyl-2-thiazolines(I) undergo two types of photoreactions, rearrangement to N-alkenylthioamides(II and III) and [σ2 + σ2] cyclo-reversion to an episulfide and a nitrile (reaction iii), as shown in a general scheme below. Longer-wave-length light from a high-pressure mercury lamp through Pyrex was ineffective to both types of reactions; thus Ia was recovered unchanged under the conditions.



Although the synthesis of several N-alkenylthioamides has been reported by Smith and Sullivan,[10] the present photoreaction of 2-alkyl-2-thiazolines provides a new synthetic method for them, especially for N-vinylthioamides which were unknown so far. However, 2-thiazolines having a substituent allowing resonance interaction with the thiazoline chromophore, such as 2-phenyl, 2-styryl-, 2-(β-pyridyl)-, and 2-mercapto-2-thiazolines, were inert to photolysis under similar conditions. 2-Thiazoline itself underwent complex photoreaction to yield an unexpected product in low yield which is believed to be N-thioformylthiazolidine.

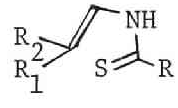
Mechanistic consideration.

At first sight, the transformation of 2-alkyl-2-thiazolines Ia,

Table 1. Photolysis of 2-thiazolines.

2-Thiazolines		Irrad. conditions		Products (% yield)[b]		
		Concn. (M/l)[a]	Time (hr)	Thioamide	Others	Recovered (%)
Ia	2-Me	0.25	87	IIa(25)	n.d.[c]	n.d.
		0.31	61	IIa(17)	(2)	65
Ib	2-Et	0.15	74	IIb(25)	n.d.	25[d]
		0.29[#]	66	IIb(14)	EtCN(9)	68
Ic	2-$PhCH_2$	0.15	62	IIc(17)	$PhCH_2CN$(13)	68
Id	2,4-Me_2	0.18	68	trans-IId(10) cis-IId(10) IIId(1)	n.d.	21[d]
Ie	2,5-Me_2	0.25	72	trans-IId(8) cis-IId(8) IIId(3)	n.d.	20[d]
If	2,4,4-Me_3	0.22	67	IIf(10) IIIf(12)	n.d.	23[d]
Ig	2,5,5-Me_3	0.18	70	IIf(16) IIIf(17)	n.d.	20[d]

a) MeCN was used as solvent except # (Et_2O). b) Yields are based on the starting 2-thiazolines. c) Not determined.
d) A considerable amount of the recovered 2-thiazoline was lost during evaporation of the solvent, because a special care was not taken.



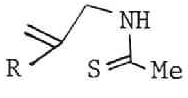
IIa: R=Me, R_1=R_2=H

IIb: R=Et, R_1=R_2=H

IIc: R=$PhCH_2$, R_1=R_2=H

IId: R=R_1=Me, R_2=H (cis and trans)

IIf: R=R_1=R_2=Me

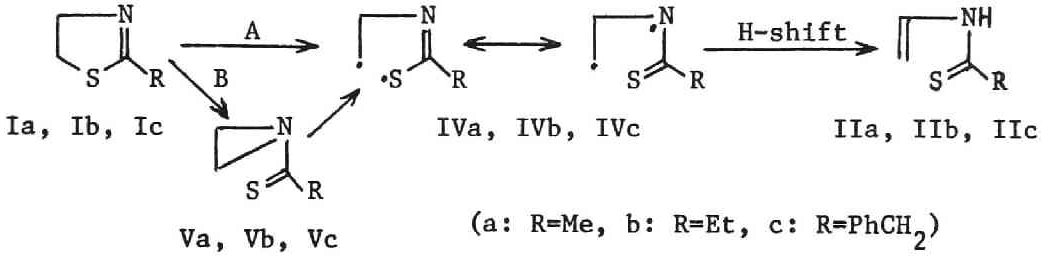


IIId: R=H

IIIf: R=Me

Ib, and Ic into IIa, IIb, and IIc respectively appeared to proceed through a biradical IV formed by C(5)-S bond fission[#] followed by hydrogen shift from C(4) to N (path A in Scheme 3). However, by analogy with the photochemical valence tautomerization of 4,5-dihydrofuran (reaction i of Scheme 2),[4] a mechanism involving a thioacylaziridine intermediate V, which can be formed directly from Ia, Ib, and Ic (path B in Scheme 3), is also attractive.

Scheme 3

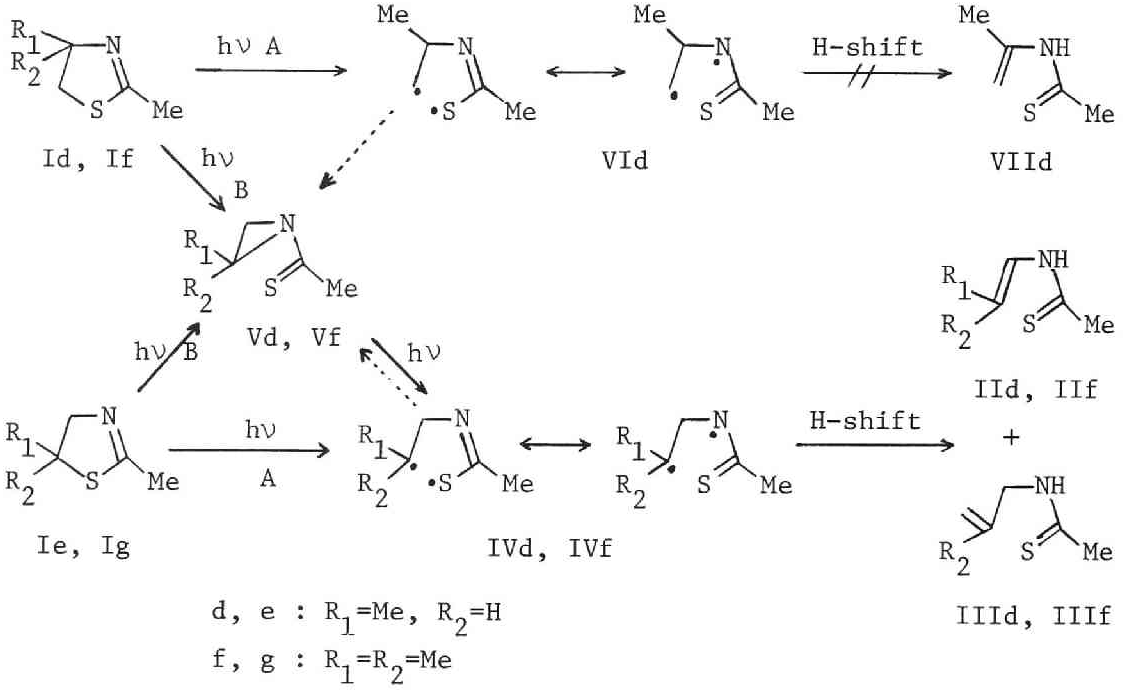


The occurrence of the latter pathway (B) is evidently demonstrated by the photorearrangement of two sets of isomeric 2-thiazolines, Id and Ie or If and Ig. Scheme 4 summarizes possible pathways for the photorearrangement of these 2-thiazolines. Both Id and Ie gave the same products, trans-IId, cis-IId, and IIId, in a similar ratio. Similarly, either If and Ig gave the same products, IIf and IIIf, in nearly the same ratio. The results indicate that Id and Ie (or If and Ig) should rearrange to the final products through a common thioacetylaziridine

[#] The C(5)-S bond is supposed to be the weakest bond in the ring. A zwitterionic species (• = +, - in IV) may also be a candidate for the intermediate.

Vd (or Vf) followed by cleavage to a biradical species IVd (or IVf) and by subsequent intramolecular hydrogen shift. It was also confirmed by NMR analysis of the photolyzate that no interconversion between Id and Ie and between If and Ig takes place during photolysis. This suggests that the thioacetylaziridine formation must be an irreversible process.

Scheme 4



There are two possible routes to the aziridine intermediate V ; namely concerted [σ2 + σ2] cycloaddition (path B in Scheme 4) and stepwise pathway via a biradical species such as I→VI→V or I→IV→V. The concerted process may be more probable, since in the photolysis products from Id N-isopropenylthioacetamide(VIId) could not be detected, which is the expected product if the biradical VId is once formed. It has been reported that the photochemical transformation of 4,5-di

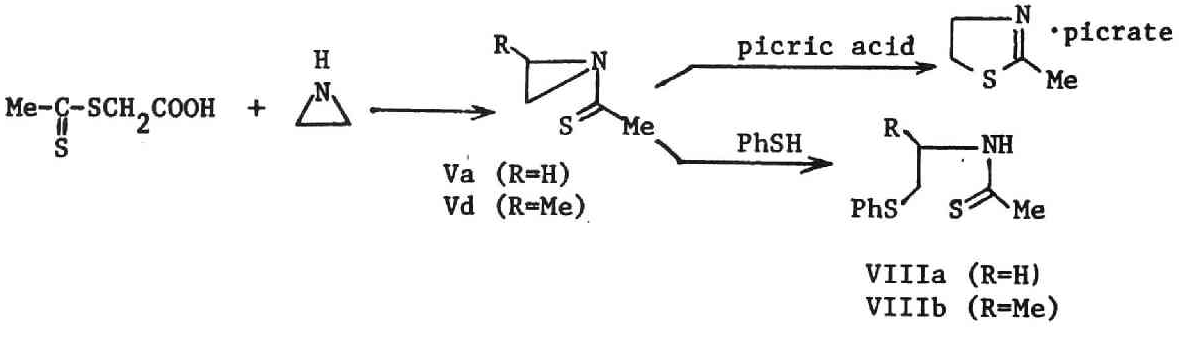
hydrofuran into formylcyclopropane involves a concerted process in part.[4f]

Evidences for the involvment of N-thioacylaziridine intermediate V.

In order to obtain further evidences for the intermediary formation of the N-thioacylaziridine V, N-thioacetylaziridine(Va) was synthesized from carboxymethyl dithioacetate and ethylene imine by applying the procedure employed for the synthesis of N-thioaroylaziridine,[11] and its chemical behaviors were examined. The aziridine Va was considerably unstable, so that it could not be obtained in a pure state. However, NMR analysis of the carbon tetrachloride extract from the reaction mixture showed signals at τ 7.42 (s, 3H, Me) and 7.49 (s, 4H, $\underset{\diagdown N \diagup}{CH_2-CH_2}$)[11] besides signals of impurities, indicating that it contained 40-65 % of Va in several experiments. Although Va decomposed gradually even at -20° to give a complex mixture of products, the production of IIa was not observed in the temperature range between -20° and 50°. Reaction of Va with picric acid and thiophenol gave expectedly[11] the picrate of Ia (nearly quantitatively) and N-(β-phenylthioethyl)thioacetamide (VIIIa; 65 % yield), respectively.

Irradiation of an ether solution of the crude Va with light at 2537 Å under cooling with ice-water gave IIa in 63 % yield, while under similar conditions without light it showed no significant change. A control irradiation experiment with Ia under the similar conditions was also carried out, and it was found that the conversion of Ia into IIa was very slow compared with the phototransformation of Va into IIa. Therfore, a pathway, by which Va rearranges to IIa via Ia can be ruled out.

In order to obtain more direct evidences for the formation of the N-thioacylaziridine V during the photolysis of 2-thiazolines I, attempts were made for trapping of Va during irradiation of Ia. After a solution of Ia in acetonitrile had been photolyzed below 5° for a short time, the NMR spectrum of aliquots was measured. Three sharp singlets attributable to the methyl and methlene protons of Va and to the methyl protons of IIa were observed between τ 7.51 and 7.62. On further irradiation the intensity of the methyl signal of IIa increased, while that of the methyl and methylene signals of Va was kept constant. Addition of thiophenol, which reacted with neither Ia nor IIa, to the photolysate resulted in the formation of the adduct VIIIa. Similarly the adduct VIIIb was obtained by treatment of the photolysate of Ie with thiophenol, indicating the formation of Vd.



The above results led me to conclude that the photorearrangement of 2-thiazolines I proceeds via N-thioacylaziridines V which are photochemically transformed into N-alkenylthioamides II and III.

3. Experimental

All the melting points are uncorrected. NMR spectra were taken on a NEVA EM-360 or T-60 spectrometer with TMS as an internal standard. IR, UV and mass spectra were taken on a JASCO IRS spectrometer, a JASCO ORD/UV-5 spectrometer, and a Hitachi RMS-4 spectrometer, respectively. Vapor phase chromatography (vpc) was carried out with a Shimadzu GC-2C using helium as carrier gas. Column chromatography (cc) was carried out on Mallinckrodt silica gel (100 mesh). Thin layer chromatography (tlc) was performed on Merck Kieselgel GF_{254} using UV light and iodine vapor for compound detection.

Preparation of 2-thiazolines.

2-Methyl-(Ia), 2-ethyl-(Ib), 2,5-dimethyl-(Ie), 2,4,4-trimethyl-(If), 2,5,5-trimethyl-(Ig), 2-phenyl-, and unsubstituted 2-thiazolines were prepared according to the Wenker's method,[12] 2,4-dimethyl-2-thiazoline(Id) according to the method of Lowell and Helmkamp,[13] and 2-benzyl-(Ic), 2-(β-pyridyl)-, and 2-styryl-2-thiazolines according to the method of Kuhn and Drawert.[14] The purity of 2-thiazolines prepared was over 98 % by NMR except Id (96 %). 2-Mercapto-2-thiazoline was commercially available.

General procedure for irradiation and product isolation.

Irradiations were performed with an acetonitrile solution of I with a 10 W low-pressure mercury lamp (Vycor housing) under bubbling nitrogen and external cooling with tap water, unless otherwise specified. After removing the solvent under reduced pressure, products were isolated by cc and preparative tlc using benzene as an eluent. For volatile products special procedures were taken. In attempts to recover the unreacted 2-thiazolines, it was found that they were mostly hydrolyzed on silica gel during elution with chloroform-acetone, reflecting their instability under acidic conditions.[15] Spectral properties of II and III, which are new compounds except IIId and IIIf,[10] are summarized in Table 2.

N-Vinylthioacetamide (IIa).

From the photolysate of Ia (5.64 g/220 ml; 87 hr), 1.39 g of IIa was isolated by cc (100 g silica gel; 1900 ml benzene) and purified by tlc, bp 70° (bath temp)/2 mmHg. (Found : C, 47.56; H, 7.26; N, 13.93; S, 31.40; C_4H_7NS requires C, 47.52; H, 6.98; N, 13.86; S, 31.65 %).

A mixture of 360 mg of IIa, 50 ml 0.1N HCl, and a few drops of MeOH was maintained at 56-60° for 4 hr. After cooling, the mixture was extracted with 50 ml ether and the ethereal layer was dried over anhydrous Na_2SO_4. Evaporation of ether gave 115 mg (43 %) of thioacetamide, mp 112-114° (from $CHCl_3$-petroleum ether) [lit[16] 113-114°], identical with an authentic sample (NMR and IR). Acetaldehyde concurrently evolved was led to a 2,4-dinitrophenylhydrazine-H_2SO_4 reagent to give its 2,4-dinitrophenylhydrazone in 45 % yield, mp 154-161° (from EtOH) [lit[17] 162°], identical with an authentic sample (IR). The above result indicates that IIa has an enamine moiety.[18]

Ethylene sulfide.

The photolysate of Ia (8.10 g/220 ml; 61 hr at ca. 10°) was distilled through a Widmer fractionating column. From the distillate (3.5 ml) up to 80°, ethylene sulfide was separated by vpc (PEG 20M; 20 % ; 40-60 mesh; 0.5 atm/cm^2 gauge; at 50) in 2 % yield, which was identified by vpc retention time and IR. The yield of IIa and the recovered Ia were determined by UV analysis of the photolysate.

N-Vinylthiopropionamide (IIb).

From the photolysate of Ib (3.70 g/220 ml; 74 hr), 900 mg of IIb was isolated by cc (80 g silica gel; 1300 ml benzene) and purified by tlc, bp 90° (bath temp)/ 4 mmHg. (Found : C, 51.87; H, 7.84; N, 11.90; S, 27.50; C_5H_9NS requires : C, 52.16; H, 7.88; N, 12.17; S, 27.79 %).

Propionitrile.

The photolysate of 7.31 g of Ib in 220 ml ether (66 hr) was evaporated through a Vigroux column to remove most of the solvent. Distillation of a part of the residue afforded propionitrile identified by vpc retention time (Silicone DC 550; 0.4 atm/cm^2 gauge; at 60°) and IR. The yield (9 %) was determined by vpc. From the rest of the

residue, ether was carefully removed under reduced pressure, and the yields of IIb and the recovered Ib were determined by NMR with adding 2-methylimidazole as an internal standard.

N-Vinylthiophenylacetamide (IIc).

From the photolysate of Ic (6.01 g/220 ml; 62 hr), 1.01 g of IIc and 0.75 g of benzyl cyanide were successively isolated by cc (110 g silica gel; 1300 ml benzene). Benzyl cyanide was identical with an authentic sample (IR). Recrystallization of IIc from ligroin gave colorless crystals, mp 91.5-92.5°. (Found : C, 67.17; H, 6.00; N, 8.09; S, 18.30; $C_{10}H_{10}NS$ requires : C, 67.78; H, 6.28; N, 7.91; S, 18.06 %).

N-(cis-1-Propenyl)- and N-(trans-1-propenyl)thioacetamides (cis- and trans-IId) and N-allylthioacetamide (IIId).

From the photolysate of Id (4.17 g/200 ml; 68 hr), 420 mg of cis-IId, 420 mg of trans-IId, and 40 mg of IIId were successively isolated by cc (80 g silica gel; 4100 ml benzene). Careful inspections of NMR spectra of the photolysate and the cc fractions showed no signals attributed to Ie and expected for VIId. IIId was identical with an authentic sample obtained by an independent synthesis.[10] Distillation of cis-IId gave an oil, bp 80-90° (bath temp)/3 mmHg, which crystallized on standing, mp 40-42°. (Found : C, 52.33; H, 8.01; N, 12.26; S, 27.92; C_5H_9NS requies : C, 52.16; H, 7.88; N, 12.17; S, 27.79 %). Distillation of trans-IId gave an oil, bp 90-95° (bath temp)/3 mmHg. (Found : C, 51.86; H, 8.02; N, 11.99; S, 27.53. C_5H_9NS requires : C, 52.16; H, 7.88; N, 12.17; S, 27.79 %).

The photolysis of Ie (6.50 g/220 ml; 72 hr) gave a similar result (Table 1).

N-2-Methyl-1-propenylthioacetamide (IIf) and N-2-methylallylthioacetamide (IIIf).

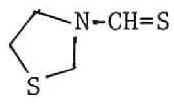
NMR analysis of the photolysate of If (6.17 g/220 ml;67 hr) showed no interconversion between If and Ig during photolysis. From the photolysate 620 mg of IIf and 740 mg of IIIf were successively obtained by cc (silica gel 140 g; 5500 ml benzene). Distillation of IIf gave an oil, bp 55-65° (bath temp)/2 mmHg. (Found : C, 55.55; H, 8.71; N, 10.64; S, 24.51; $C_6H_{11}NS$ requires : C, 55.79; H, 8.58; N, 10.85;

S, 24.78 %). Distillation of IIIf gave an oil, bp 85-100°(bath temp)/ 4 mmHg, which was identical with an authentic sample (IR).[10,#]

The photolysis of Ig (5.16 g/220 ml; 70 hr) gave a similar result (Table 1).

N-Thioformylthiazolidine.

From the photolysate of 2-thiazoline (5.00 g/220 ml; 70 hr), 60 mg of the titled compound was obtained by cc (silica gel 100 g; 2100 ml benzene) and tlc (50:1 benzene-AcOH) as an oil, bp 125-130°(bath temp)/3 mmHg. $\tau(CDCl_3)$ 0.68 (1H, sharp signal with very fine splitting, -CH=S)[19] 5.19 (2H, sharp singlet with very fine splitting, S-CH_2-N), 5.74-6.04 (2H, m, SHC-N-CH_2-CH_2-), 6.68-6.96 (2H, m, -S-CH_2-CH_2-); ν_{max}(Neat) 1480, 1230, 1155, 1110 cm^{-1} (-CS-N-)[20]; λmax (EtOH) 272 nm (ε 15900) ; m/e 133 (rel. int. 100, M^+), 54 (57), 45 (70), 28 (77). The spectral data are consistent with the following structure. (Found : C, 36.34; H, 5.45; N, 10.55; S, 47.82; C_4H_7NS requires : C, 36.09; H, 5.30; N, 10.52; S, 48.08 %).



N-Thioacetylaziridine (Va).

The known synthetic procedure for thioacylaziridine[11] was applied for the preparation of Va. To a solution of carboxymethyl dithioacetate[21] (300mg) and sodium bicarbonate (190 mg) in water (1 ml) was added ethylene imine (0.16 ml) in water (1 ml) under ice-cooling. The reaction mixture was extracted with CCl_4 (total 10 ml). The organic layer was washed with ice-water, dried over anhydrous Na_2SO_4, and immediately submitted to NMR analysis. It showed two singlets at τ 7.42 (Me protons) and 7.49 (aziridine protons)[11] in addition to many low-intensity signals owing to impurities. For several preparation, the yield of Va was estimated to be 20-30 % and the purity of Va in the CCl_4 extracts to be 40-65 % by NMR integration.

The authors wish to thank Professor P. A. S. Smith for sending the IR chart of IIIf.

Reaction of Va with picric acid.

To 3 ml of the above CCl_4 extract was added picric acid (100 mg) and the mixture was refluxed for 3 hr, giving yellow precipitates which were separated by filtration and recrystallized from benzene-EtOH to give 2-methyl-2-thiazoline picrate (65 mg) in almost quantitative yield, mp 155-170° [lit[12] 171°], identical with an authentic sample (IR).

N-2-Phenylthioethylthioacetamide (VIIIa).

To 5 ml of the above CCl_4 extract was added thiophenol (0.1 ml) and the mixture was stirred for 2 hr at room temperature and for additional 2 hr at 50-60°. Evaporation of the solvent gave a yellow oil (220 mg), from which 36 mg (65 %) of VIIIa was isolated by preparative tlc (silica gel/$CHCl_3$) followed by distillation as an oil, bp 110-140° (bath temp)/10^{-4} mmHg. τ(CCl_4) 1.97 (1H, broad, NH), 2.53-2.95 (5H, m, aromatic protons), 6.22 (2H, slightly split q, became slightly split t by adding D_2O, J_{CH-CH}=6Hz, J_{CH-NH}=6 Hz, -NH-C<u>H</u>$_2$-CH_2-), 6.87 (2H, slightly split t, J_{CH-CH}=6 Hz, -S-C<u>H</u>$_2$-CH_2-), 7.58 (3H, s, C<u>H</u>$_3$-CS-); ν_{max}(Neat) 3300 (NH), 1535, 1150 (-CS-NH-), 740, 695 (Ph-) cm^{-1}. (Found : C, 56.67; H, 6.26; N, 6.46; $C_{10}H_{13}NS_2$ requires : C, 56.86; H, 6.20; N, 6.63 %).

Photolysis of N-thioacetylaziridine (Va).

One-sixth of the reaction mixture prepared from carboxymethyl dithioacetate (325 mg), ethylene imine (0.17 ml), sodium bicarbonate (210 mg), and water (2.5 ml) as above was extracted with 0.4 ml CCl_4. NMR analysis of the extract showed that it contained Va in 40 % purity. The rest of the reaction mixture was extracted with 5 ml ether, in which the content of Va was found to be almost same as in CCl_4. Three-fifth of the ether extract was transferred into a quartz tube, which was closed after nitrogen bubbling and then irradiated externally (2537 Å light) under cooling with ice-water for 2 hr. NMR spectra of the photolysate and the rest of the ether extract kept in the dark were measured after evaporating ether at low temperature in vacuo followed by dissolving the residues in $CDCl_3$. Comparison of the spectra indicated that on irradiation 46 % of Va (τ 7.43 and 7.48) was recovered and

67 % of the reacted Va was converted into IIa (τ 7.48, 5.01-5.47). The NMR signals corresponding to 2-methyl-2-thiazoline were not observed. IIa was isolated by preparative tlc (silica gel; 50:1 $CHCl_3$-acetone), which was identical with an authentic sample (IR). The yield (63 %) was in good agreement with that estimated from NMR analysis.

A control experiment with Ia (0.1 ml in 10 ml ether) was carried out under the same irradiation conditions. After evaporating the photolysate at low temperature in vacuo, NMR analysis (CCl_4) of the residue showed that it consisted of a large amount of the recovered Ia (ca. 97 %),IIa (ca. 2 %), and Va (ca. 1 %), demonstrating that the photoreaction of Ia is very slow compared with that of Va.

Trapping of Va from the photolysate of Ia.

A solution of Ia (6.13 g) in 220 ml acetonitrile was irradiated internally at 1-5°. Aliquots of the photolysate were withdrawn at time intervals 4, 13, and 23 hr. After removing most of the solvent at room temperature in vacuo, each residue was analyzed by NMR (CCl_4), which showed the signals of Va at τ 7.51 and 7.57 and of IIa at 7.62. These signals appeared at somewhat higher field than those measured in pure CCl_4, probably due to the solute-solute interactions. To the photolysate after 23 hr irradiation was added thiophenol (2 ml) and the mixture was stirred 2 hr at room temperature, then 2 hr at 55-66°. The solvent was removed and the residue was separated by preparative tlc (silica gel; $CHCl_3$) to give VIIIa (100 mg) which was identical with an authentic sample (IR). As a control experiment a mixture of Ia (28 µl) and IIa (28 mg) were treated with thiophenol (28 µl) in 1 ml acetonitrile as above to give no VIIIa (tlc and NMR) but the recovered starting materials.

Trapping of Vd from the photolysate of Ie.

Similar treatment of the photolysate of Ie (5.35 g) in 220 ml acetonitrile after 18 hr irradiation with thiophenol (2 ml) yielded VIIIb (50 mg) as an oil ; bp 150-165°(bath temp)/10^{-4}mmHg ; τ (CCl_4) 2.16 (1H, broad d, J_{NH-CH}=7 Hz,-NH-CH-), 2.45-3.02 (5H, m, C_6H_5-), 5.27 (1H, broad septet, became broad sextet by adding D_2O,J_{CH-NH}=7 Hz,

J_{CH-CH_3}=6.5 Hz, J_{CH-CH_2}=5.5 Hz, -NH-C$\underline{H}$(CH_3)-CH_2-), 6.87 (2H, d, J_{CH_2-CH}= 5.5 Hz, -C$\underline{H}_2$-CH-), 7.74 (3H, s, C$\underline{H}_3$-CS-), 8.72 (3H, d, J_{CH_3-CH}=6.5 Hz, C$\underline{H}_3$-CH-) ; ν_{max}(neat) 3230 (NH), 1535,1115 (CS-N), 740, 685 (Ph) cm^{-1}. (Found : C, 58.93; H, 6.94; N, 6.49; $C_{11}H_{15}NS_2$ requires : C, 58.65; H, 6.71; N, 6.22 %).

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Table 2. Spectral data of thioamides II and III.

Thioamides	τ, [Solvent], J(Hz)[a]			
	CH_3CS- (3H, s)	NH (1H, br)	=CH-NH- (1H)	Others
IIa	7.40	0.20 [CCl_4]	2.30-2.86 (dq,[b] J=10)	4.80-5.34 (2H,q, $-CH=CH_2$)[c]
IIb	7.27 (2H,q,J=7, $-CH_2CH_3$)	0.88 [$CDCl_3$]	2.21-2.80 (dq,J=10)	4.83-5.29 (2H,q, $-CH=CH_2$)[c] 8.67 (3H,t,J=7, $-CH_2CH_3$)
IIc	5.87 (2H,s, CH_2Ph)	1.47 [$CDCl_3$]	2.20-2.81 (6H,m[d])	5.04-5.34 (2H,m, $-CH=CH_2$)[c]
cis-IId	7.40	0.90 [CCl_4]	2.65-3.05 (tm,[e] J=9.5)	4.91 (1H,br quintet, $J^{cis}_{-CH=CH-}$=9, $J_{=CHCH_3}$=8, $-CH=CHCH_3$) 8.23 (3H,dd, $J_{-CH=CCH_3}$=1.5, $-CH=CHCH_3$)
trans-IId	7.47	0.08 [CCl_4]	2.55-3.03 (tm,[e] J=9.5)	4.36 (1H, sextet, $J^{trans}_{-CH=CH-}$=14, $J_{=CHCH_3}$=7, $-CH=CHCH_3$) 8.24 (3H,dd, $J_{-CH=CCH_3}$=1.5, $-CH=CHCH_3$)
IIf	7.39	1.07 [$CDCl_3$]	3.01 (dm,[f] J=9)	8.21 (6H,d,J=1.5, $-CH=C(CH_3)_2$)

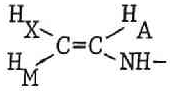
	ν_{max}^{neat} (cm^{-1})		m/e (Rel. int.)[h]	λ_{max}^{EtOH} (ε)
NH	C=C	CS-N		nm
3200	1630,975	1510	101(100, M^+), 100(97)	300
	880	1130	59(80), 43(52), 42(46)	(15700)
3250	1645,960	1515	115(100, M^+), 114(95)	300
	865	1120	73(81, $EtC{=}S^+$), 45(81)	(19100)
3250	1635,970	1520	177(66, M^+), 176(60)	303
	890	1110	134(62), 91(100, $C_7H_7^+$) 59(60)	(18000)
3260	1670,725	1510	115(86, M^+), 100(100)	300
		1105	59(87), 56(70), 42(62)	(21600)
3250	1675,940	1530	115(46, M^+), 100(100)	300
		1115	59(85), 56(57)	(24500)
3250	1645,825	1515	129(17, M^+), 114(80)	300
		1130	59(78)	(17300)

Table 2. (continued)

Thioamides	τ, [Solvent], J(Hz)[a] CH_3CS- (3H, s)	NH (1H, br)	=CH-NH- (1H)	Others
IIId	7.48	1.93 [CCl_4]	—	3.81-4.35 (1H,m,-CH=CH_2), 4.55-4.93 (2H,m, -CH=CH_2), 5.76 (2H,tm,[e] J_{-CH_2NH-}=6, J_{-CH_2-CH-}=6, -NHCH_2-)
IIIf	7.36	1.96 [$CDCl_3$]	—	5.06 (2H,m, $CH_3C=CH_2$), 5.70 (2H,br d,[g] J_{-CH_2NH-}=6, -CH_2NH-), 8.19 (3H,br s, $CH_2=CCH_3$)

a) s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

b) Became q by adding D_2O.

c) Interpreted as an AMX,  : 2.58(H_A), 4.94(H_M), 5.27(H_X), J_{AM}=16 Hz, J_{AX}=9 Hz, J_{MX}=0 Hz (IIa). Similar interpretations were done for IIb and IIc.

d) Overlapped with Ph protons.

e) Became br d by adding D_2O.

f) Became m by adding D_2O.

g) Became br s by adding D_2O.

	ν_{max}^{neat} (cm^{-1})		m/e (Rel. int.)[h]	λ_{max}^{EtOH} (ε)
NH	C=C	CS-N		nm
3300	1645,940	1535 1170	—	—
3250	1655,930	1530 1170	129(13, M^+), 114(88) 59(50), 42(68)	267 (16700)

h) A peak at m/e 59 is assigned for $CH_3-\overset{+}{C}=S$.

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C H A P T E R II

The Photochemistry of 2-Isoxazolines

Upon irradiation with 253.7 nm light, 2-isoxazolines undergo three types of formal [2 + 2] cycloreversions in addtion to 1,2-bond cleavage followed by further transformation (Cf. Table 1). For example, 3,5-diphenyl-2-isoxazoline gave benzonitrile (type iii product), 4,5-diphenyl-3-oxazoline and benzaldehyde (type iv product), styrene (type v product), and β-aminochalcone and 2-phenylquinoline (1,2-cleavage product). 4,5-Diphenyl-3-oxazoline was shown to be formed via fragmentation into 2-phenylazirine and benzaldehyde followed by photochemical recombination, and 2-phenylquinoline via 1,2-bond cleavage followed by recyclization. In order to know whether the localized excitation of a particular chromophoric group is responsible for each type of reaction in such unconjugated polychromophoric compounds, the effects of sensitizer, quencher and excitation wave-length were examined with selected 2-isoxazolines. It is suggested for 2-isoxazolines having a phenyl ketoxime group and a 4-aryl or/and 5-aryl group that an excited singlet state of 4- or 5-aryl group is responsible for the formation of type iv products and an excited singlet state of the phenyl ketoxime group for that of type v products.

1. Introduction

In the preceding chapter,[1] the author has described the photochemical reaction of 2-thiazolines occurring *via* formal [2 + 2] cycloreversions, reactions *i* and *iii*, among five types of [2 + 2] reactions (*i*-*v* in Scheme 2[#] of the preceding chapter) possible for five-membered dihydroheteroaromatics. In this chapter the author describes the full detail of the photochemistry of 2-isoxazolines involving [2 + 2] reactions *iii*, *iv* and *v* as well as other types of cleavage reactions.

2. Results and Discussion

Photolysis products of substituted 2-isoxazolines.

When a solution of 2-isoxazolines **1**, **5**, **6**, **8**, **11** and **13** in acetonitrile were irradiated with light mainly at 2537 Å, they gave various products which are listed in Table 1 by classifying into those attributable to [2 + 2] reactions, *iii*, *iv* and *v* and other types. 3,5-Diphenyl-2-isoxazoline(**1**) produced 4,5-diphenyl-3-oxazoline(**2**)and β-aminochalcone as already reported by Schmid et al[2], in addition to 2-phenylquinoline(**3**), benzonitrile, benzaldehyde and styrene. Irradiation of other substituted 2-isoxazolines **5**, **6**, **8**, **11** and **13** gave products analogous to those from **1**. Among these products, acetonitrile

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[#] The designations used for the type of reaction in the preceding chapter[1] are employed throughout this paper.

oxide, which was trapped as 3-methyl-4,5-trimethylene-2-isoxazoline[3] by irradiating 5 in the presence of cyclopentene in an ether solution, is regarded as an equivalent of 3-methyloxazirine which is expected to form together with stilbene from 5 by reaction v.

The results indicate that the product distribution are largely depending upon substituents. Reaction iii occurred in a small or no extent and the counterpart product (an epoxide) could not be detected. Reaction iv occurred in most cases but reaction v was much predominant in the cases of 4,5-disubstituted 2-isoxazolines. Involvement of reaction iv in the skeletal rearrangement of 1, 6 and 8 into 2, 7 and 9, respectively, will be discussed below.

Mechanistic consideration.

For the skeletal rearrangement of 1 into 2, following three pathways were taken into consideration (Scheme 1) : (1) Recombination of 2-phenylazirine and benzaldehyde formed by reaction iv, as originally proposed by Schmid et al,[2] (2) recombination of benzonitrile and styrene oxide formed by reaction iii, and (3) type ii rearrangement of 3,4-diphenylisoxazoline(8) formed through valence tautomerization involving reaction i.

Scheme 1

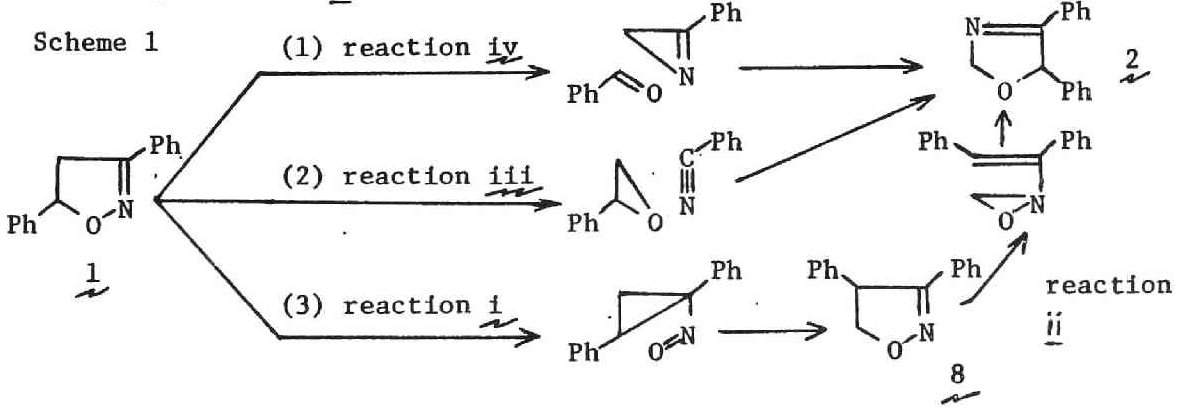
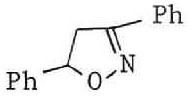
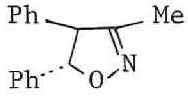
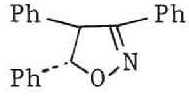
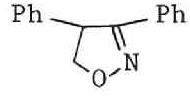
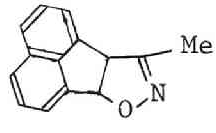
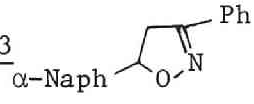
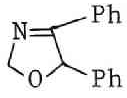
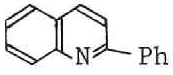
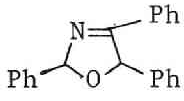
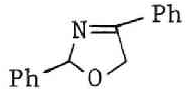
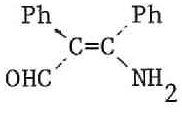
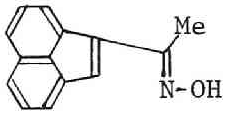


Table 1. Photolysis products from 2-isoxazolines

	Compound	Concn. (x 10^2 M/L)	Irrad. time(hr)	Recovered (%)	Type iii
1		4.0	24	24	PhCN (2.0)
5		4.3	24	59	—
6		3.3	25	31	PhCN (0.6)
8		3.6	24	trace	—
11		4.7	29	79	—
13		4.6	62	49	—

a) Yields were calculated on the basis of the reacted starting material.

b) Cis : trans = 1 : 1.

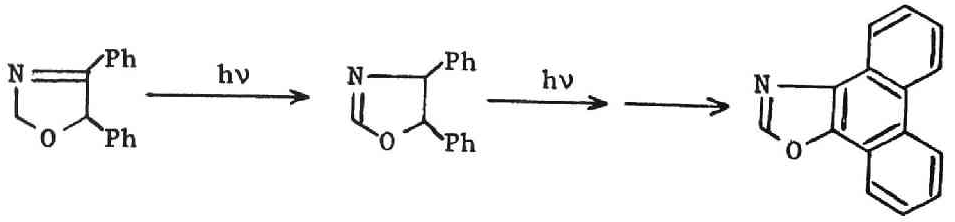
Products (% yield)[a]		
Type iv	Type v	Others
2  (19)	$PhCH=CH_2$ (1.6)	3  (15)
PhCHO (1.1)		$PhCOCH=C(NH_2)Ph$ 4 (3)
PhCHO (1.0)	PhCH=CHPh[b] (66) $MeC{\equiv}N{\rightarrow}O$[c] (29)	—
7[d]  (28)	PhCH=CHPh[e] (39)	—
PhCHO (0.7)		
9  (6)	—	10  (86)
—	 (57)	12  (9)
α-Naph-CHO (12)	α-Naph-$CH=CH_2$ (16)	—

c) Trapped as a cyclopentene adduct (see text).

d) Cis : trans[4] = 1.6 : 1 .

e) Cis : trans = 2 : 1 .

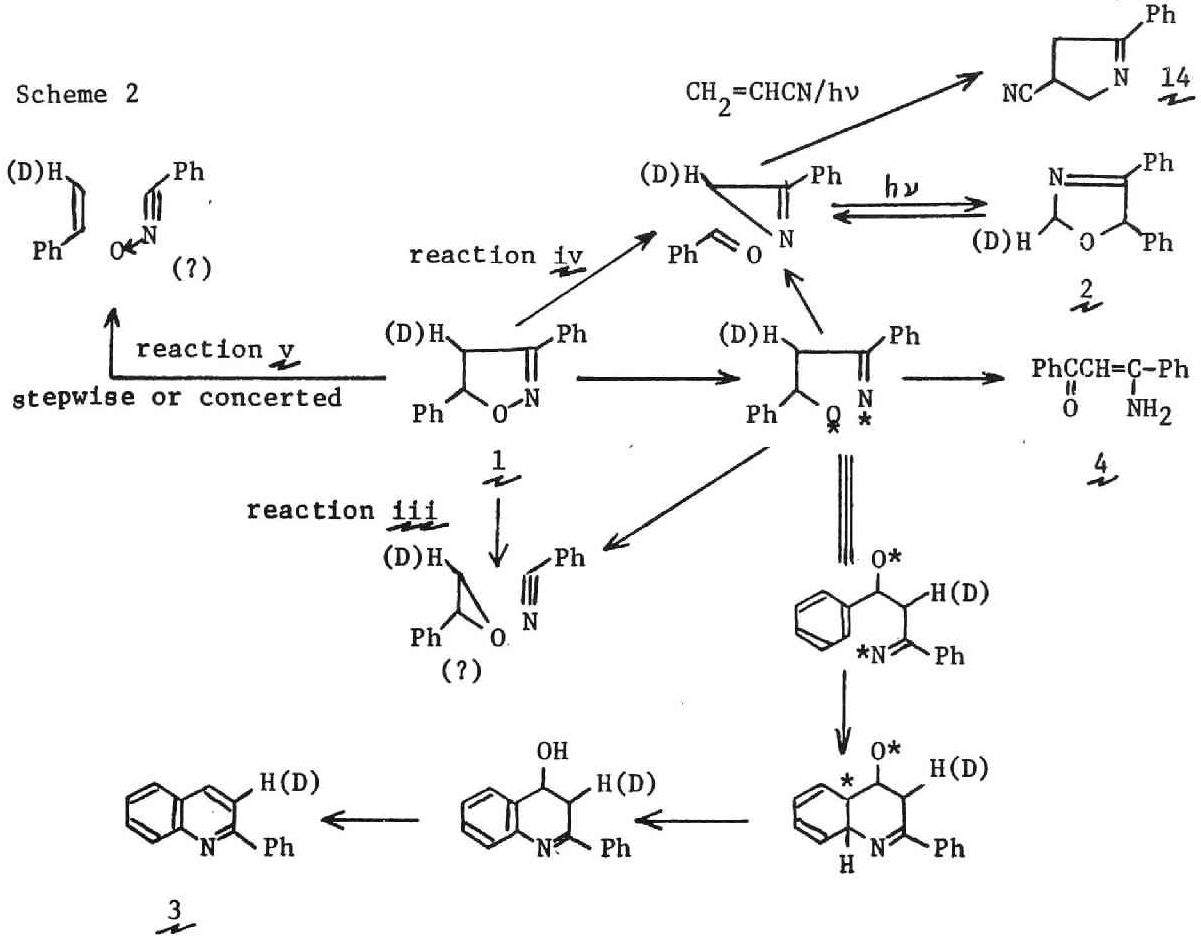
Path (2) was eliminated by the fact that even a trace of 2 could not be detected when a mixture of styrene oxide and benzonitrile was either irradiated under similar conditions or allowed to stand in the dark. Path (3) was also eliminated because irradiation of 8 gave 9 and 10 but not 2 (Table 1). Path (1) had been supported by the fact that irradiation of an equimolar mixture of 2-phenylazirine and benzaldehyde afforded 2,[2] which was also confirmed independently by the author. A similar photochemical formation of 3-oxazolines has been also recently reported.[4] Unfortunately it was unsuccessful to detect the intermediate 2-phenylazirine by following the photochemical reaction of 1 by IR spectroscopy, as was expected from the finding that 2-phenylazirine and benzaldehyde photochemically reacted much faster than the conversion of 1 into 2. However, irradiation of both 1 and 2 in the presence of a large excess of acrylonitrile gave 2-phenyl-4-cyano-1-pyrroline(14)[5] in 29 and 42 % yields, respectively, indicating that [2 + 2] cycloreversion into phenylazirine and benzaldehyde occurred with both 1 and 2. On prolonged irradiation 2 gave a complex mixture of products including benzoic acid (17 %) and phenanthro[9,10-d]-oxazole (15; 3 %). Benzoic acid may originate in benzaldehyde and 15 in 16 which can be formed by a 1,3-hydrogen shift of 2 as observed in the case of Δ^2-pyrazoline.[6]



2 16 15

All the products from reactions iii and iv as well as 4 and 10 may be attributed to the primary cleavage (homolytic or heterolytic) of the N-O bond of isoxazolines, as seen in the photoreaction of isoxazoles,[7] followed by the successive bond cleavage at the 3-4 bond (reaction iii) and at 4-5 bond (reaction iv) or by intramolecular hydrogen shift in the cases of 4 and 10. The one-step route leading to an azirine and an aldehyde or to a nitrile and an epoxide may be also possible. These pathways are shown in Scheme 2 for the photoreaction of 1.

Scheme 2

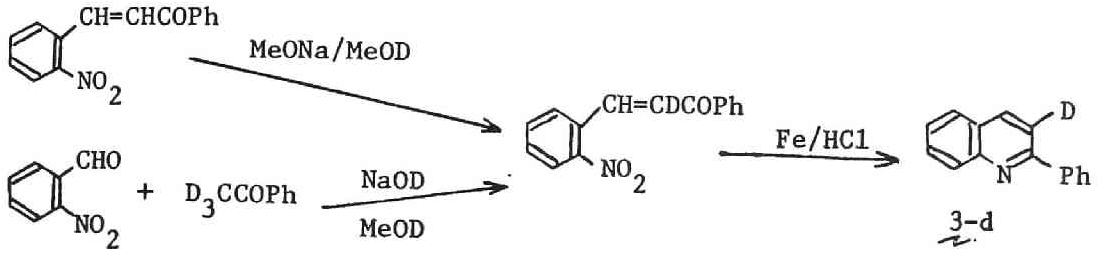


The formation of 3 from 1 can be also attributed to the primary

N-O bond cleavage, followed by the intramolecular attack of $>C=N^{*}$ group to the benzene ring of position 5 (Scheme 2). An analogous transformation has been observed in the photolysis of 3,5-diphenyl-1,2,4-oxadiazole leading to 2-phenyl-4-quinazolone.[8] This scheme was supported by a deuterium labeled experiment. Thus, irradiation of 1-d (1.3 D at position 4) under similar conditions gave 2-d (1.2 D at position 2), 3-d (1.0 D at position 3), and unlabeled benzaldehyde, and the recovered 1-d showed no deuterium scrambling. Unlabeled 3 was not detected by NMR spectroscopy, indicating that hydrogen at position 4 of 1-d had been released more predominantly than deuterium. The labeled experiment is also consistent with path (1) of Scheme 1 for the formation of 2.

The position and content of deuterium of the above products were determined by NMR analysis. Three ring protons of 2 appeared as an AB_2 pattern at τ 4.24 (B_2 part) and 4.07 (A part) with J_{AB}=5 Hz. It became clear by a comparison of the J value with those of 9 (See Experimental) that two protons at position 2 of 2 correspond to B_2 part and one at position 5 to A part. From the fact that the NMR spectrum of 2-d revealed one-protone decrease in the B_2 region, the position of deuterium was deduced to be position 2. This is also supported by the mass spectrum of 2-d showing a strong M^{+}-PhCHO peak at m/e 118 in contrast to that of 2 at m/e 117. The NMR spectrum of 3-d showed almost complete disappearance of a doublet at τ 2.25 (J=8.5 Hz) which is present for unlabeled 3. The position of deuterium was unequivocally established by a synthesis of 3-d by the reductive cyclization[9] of

2-nitrochalcone-α-d, which had been prepared by applying two known methods; namely mono-deuteration[10] of 2-nitrochalcone and condensation[11] of o-nitrobenzaldehyde with acetophenone-ω-d_3[12] as shown below.



For the formation of the fragmentation products resulted from the formal [2 + 2] reactions iii, iv and v of 2-isoxazolines (Scheme 2), there are two possible routes; namely concerted or stepwise. A definite conclution is difficult to draw from the available data. However, considering the fact that acetonitrile oxide could be trapped with cyclopentene in the photolysis of 5 but not in the case of 11, it may be supposed that type v fragmentation of 5 leading to acetonitrile oxide and stilbene takes place concertedly but that of 11 leading to acenaphthylene stepwise. The much lower yield of amino ketone 4 from 1 than amino aldehyde 10 from 8 may imply that type iv fragmentation of 1 takes place more concertedly than that of 8.

Which chromophoric unit is responsible for the photoreactions of 2-isoxazolines.

There are many report[13] on the photochemistry of bichromophoric molecules in which the chromophoric units are not directly conjugated. In the present case, it should be noted that 2-isoxazoline 6, which is trichromophoric (two phenyl and a Ph-C=N-O- groups), underwent mainly

two types of reactions, iv and v, while bichromophoric 8 did a selective reaction to give 10 in high yield. A question arises whether the localized excitation of a particular chromophor is responsible for each type of reaction or not. In order to solve this question, the effects of sensitizer, quencher, and excitation wave-length were examined with three selected compounds, 6, 8 and 13. The results are shown in Table 2

The molar absorption coefficients (ε) of these compounds are also listed in Table 2. It can be seen from the data that light through Pyrex(>ca. 290 nm) excites selectively the phenyl ketoxime (PKO) group of 6 and 8, because an alkylbenzene has no absorption over 290 nm, and that the same light excites mainly the naphthyl group of 13 (Cf. ε_{294} 7800 and ε_{316} 700 for 1-ethylnaphthalene[14]). Irradiation with a low-pressure mercury lamp with Vycor housing (mainly 253.7 nm) will cause comparative excitation of both PKO and an aryl groups at position 4 or 5 in all these compounds : compare λ_{max}(EtOH) 245 nm (ε 10000) for acetophenone oxime,[15] 261 nm (ε 7000) for 1-ethylnaphthalene,[14] and 260 nm (ε 530) for ethylbenzene.[16]

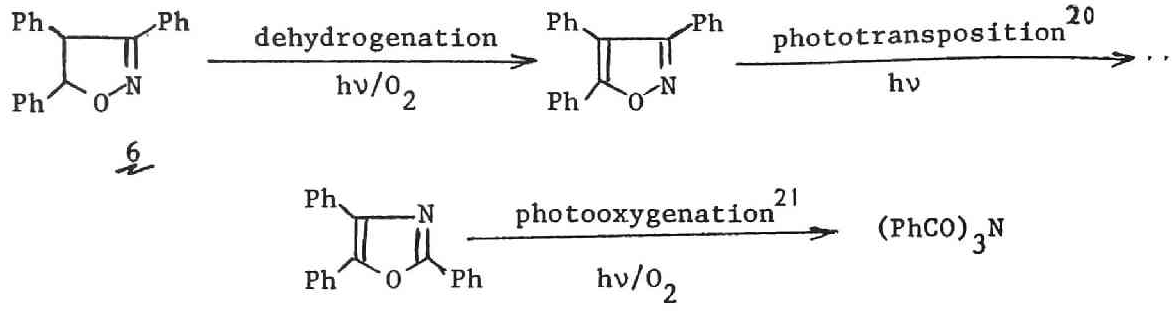
With trans-3,4,5-triphenyl-2-isoxazoline(6), the following observations were obtained : (a) On irradiation with 253.7 nm light, which can excite both PKO and 4- and 5-phenyl groups, 6 gave both type iv and v products irrespective of the initial concertration of 6 (No. 1 and 2 of Table 2). (b) Irradiation of 6 with light through Pyrex, which can excite only PKO group, yielded type v product but no type iv product regardless of reaction temperature (No. 3 and 4), indicating that the excitation of PKO group is responsible at least in part for

the formation of type v products while the excitation of a phenyl group at 4- or 5-position for the formation of type iv product. (c) The formation of type iv and type v products was neither quenched by piperylene (No. 5) nor sensitized by a triplet sensitizer such as benzophenone and xanthone (No. 6 and 7), which have a higher triplet energy, 69 and 74.2 kcal/mole respectively, than that expected for PKO group (Cf. E_T < 60 kcal/mole for benzaldoxime[17,34]). (d) Irradiation of 6 in benzene with 253.7 nm light, under conditions that 98.5 % of the the incident light is absorbed by benzene, caused efficient fragmentation into type v products (No. 8).

The experimental results, (a), (b) and (c), led the author to suggest that type v products may be formed from an excited singlet state of PKO chromophor of 6, and that reaction iv may not involve the excitation of PKO group but possibly occurs from an excited singlet state of a phenyl group at position 4 or 5. For experiment (d), benzene should act as a singlet sensitizer which may transfer the singlet energy to PKO group but not to the 4- or 5-phenyl group. There has been ample evidence for singlet sensitization with benzene,[18] including the benzene-sensitized valence isomerization of indoxazene (1,2-benzisoxazole).[19]

The formation of tribenzamide is interpreted by a following sequence of photoreactions. In fact, photooxygenation of 6 gave tribenzamide and further decomposition products (No. 9).

With 3-phenyl-5-(α-naphthyl)-2-isoxazoline (13): (a) Irradiation with 253.7 nm light gave both type iv and type v products in compara-



6

tive yields (No. 10). (b) Irradiation with light through Pyrex (more than 90 % of the incident light excites 5-naphthyl group) gave almost exclusively type iv product (No. 11), eliminating a possiblity of the participation of the excited 5-aryl group in type v reaction. (c) Xanthone-sensitization was ineffective and neither type iv nor type v product was formed (No. 12), while benzene-sensitization occurred efficiently to give both types of products (No. 13), indicating again that benzene acts as a singlet sensitizer. In accordance with the above suggestion for 6, it is also suggested that excited states of PKO and 5-naphthyl groups are responsible for the formation of type v and type iv products, respectively, and that singlet state are possibly involved in the formation of both types of products.

With 3,4-diphenyl-2-isoxazoline (8): (a) In contrast to 6 and 13, irradiation with 253.7 nm light gave type iv product in addition to 10 but no type v product (No. 14). (b) Irradiation with light through Pyrex yielded only 10 (No. 15). (c) The photoreaction was not sensitized with xanthone (No. 16). The results imply that an excited state of 4-phenyl group, possibly singlet state, is responsible for the formation

of type iv product, and that an excited singlet state of PKO group is involved in the formation of 10 at least in part.

In conclusion, it may be risky to construct a general rule for the photoreactions of 2-isoxazolines, since problems on interaction between different chromophoric units in both the ground and excited states of these molecules are still unsolved. However, considering a high substituent dependency of the product distribution, the following features are of importance for 2-isoxazolines having a PKO group and an aryl group.

1. Type iv reaction leading to products via the primary cleavage of 1,2- and 4,5-bonds occurs possibly from a singlet excited state of 4- or 5-aryl group.
2. Type v reaction leading to products via the primary cleavage of 3,4- and 1,5-bonds occurs possibly from a singlet excited state of phenyl ketoxime group.
3. The formation of 10 resulted from 1,2-bond cleavage of 8 involves at least in part a singlet excited state of phenyl ketoxime group.

3. Experimental[#]

Materials.

All 2-isoxazolines were prepared according to the literature

[#]For general descriptions, see Experimental part of the preceding chapter[1] (except a JASCO IRA-1 spectrometer for IR and a Shimadzu UV-200 spectrometer for UV).

Table 2. Photolysis of 2-isoxazolines 6, 8, 13 under various

Expt. No.	Additive	Solvent (ml)	Concn. ($\times 10^{2}$ M/L)	Irradn. conditions: Light source[b]	Irradn. conditions: Time (hr)
trans-3,4,5-Triphenyl-2-isoxazoline (6): ε_{254} 9500; ε_{300} 170; ε_{320} 0.					
1[d]	—	MeCN (220)	3.3	A	25
2	—	MeCN (1000)	0.10	A	25
3	—	MeCN (200)	3.1	B	113
4	—	MeCN (100)	3.0	B	130 at 95°
5	Piperylene (0.107M/L)	MeCN (14)	2.5	A[g]	27
6	Benzophenone (6.35×10^{-2} M/L)	MeCN (90)	3.7	B[j]	62
7	Xanthone (3.74×10^{-2} M/L)	MeCN (15)	2.1	C[g,k]	46
8	—	C_6H_6 (3450)	0.10	A	57
9	Under air	MeCN (350)	0.98	C	280
3-Phenyl-5-(α-naphthyl)-2-isoxazoline (13): ε_{254} 11700; ε_{300} 2900; ε_{320} 180.					
10[d]	—	MeCN (240)	4.6	A	62
11	—	MeCN (200)	2.1	B	46
12	Xanthone (2.56×10^{-2} M/L)	MeCN (180)	2.0	B[k]	43
13	—	C_6H_6 (1600)	0.041	A	23
3,4-Diphenyl-2-isoxazoline (8): ε_{254} 8300; ε_{300} 170; ε_{320} 0.					
14[d]	—	MeCN (100)	3.6	A	24
15	—	MeCN (15)	1.1	C[g]	34
16	Xanthone (2.96×10^{-2} M/L)	MeCN (15)	1.1	C[g,k]	50

conditions[a]

Products (% yield)[c]						
Recovered	Type iii	Type iv		Type v		Others
	PhCN	PhCHO	7	PhCH=CHPh	Phenanthrene	$(PhCO)_3N$
31	0.4	0.4	19[e]	20[f]	—	0
0	n.d.	n.d.	8	Total 27		0
82	0	0	0	0	2	1
93	0	0	0	0	4	0.9
22	n.d.	n.d.	33[h]	38[i]	0	n.d.
~98	trace	0	0	0	2	0.3
~100	0	0	0	0	0	0
38	0	0	0	23[l]	6	0
0	trace	0	0	0	0	29
						$(PhCO)_2NH$ 7
						PhCOOH 12

	PhCN	α-Naph-CHO	α-Naph-CH=CH_2
49	0	6	8
68	0	3.5	trace
81	0	0	0
7	n.d.	12	22

	PhCN	9	10
2	trace	6	86
64	n.d.	0	16
92	n.d.	0	0

Table 2. (continued)

a) The photolysis was done at room temperature, unless otherwise specified. Abbreviation n.d. denotes the compound was not determined.

b) A : 10-W low-pressure mercury lamp with Vycor housing.
B : 100-W high-pressure mercury lamp (Pyrex filter).
C : 450-W high-pressure mercury lamp (Pyrex filter).

c) Yields are based on the initial amount of the starting material. . .

d) Taken from Table 1.

e) Cis : trans = 8 : 5 .

f) Cis : trans = 2 : 1 .

g) Irradiated externally.

h) Cis : trans = 6 : 5 .

i) Cis : trans = 4 : 5 .

j) An aqueous solution of potassium biphthalate (5.0 g/L) was circulated through a cooling jacket.

k) A solution of naphthalene in isooctane (12.8 g/L) was used as a filter.

l) Cis : trans = 5 : 1 .

methods: 3,5-diphenyl- (1),[22] mp 74-75° (lit[22] 75°); 4,5-diphenyl-2-mehty- (5),[23] bp 144-146°/1 mmHg (lit[23] 137°/0.11 mmHg); 3,4,5-triphenyl- (6),[23] mp 145-146.5° (lit[24] 140-141°); 3,4-diphenyl- (8),[23] mp 121-122 (lit[23] 121-121.5°); 3-meht1-acenaphtho[1,2-d]- (11),[25] mp 138.5-139.5° (lit[25] 130°); 5-(α-naphthyl)-3-phenyl- (13),[26] bp 145° (bath temp)/10^{-4}mmHg, (lit[26] mp 62°). These compounds gave satisfactory spectral and microanalytical data. 3,5-Diphenyl-2-isoxazoline-4-d (1-d) was prepared by applying the Henrich's mehtod.[27] Thus, to a solution of chalcone (5 g) in 30 ml MeOD was added a solution of hydroxylamine hydrochloride (3 g) and KOH (5 g) in 20 ml MeOD. After refluxing for 1 hr, the mixture was filtered. The filtrate was evaporated to dryness to give a residue which was mixed with water (100 ml) and extracted with ether (100 ml) three times. The ethereal layer was dried over Na_2SO_4 and evaporated to dryness. The residue (5 g) was recrystallized from ethanol (20 ml) - ligroin (10 ml), then from ethanol to give 1-d as colorless crystals (0.8 g), mp 73-74.5°. The deuterium content was estimated by NMR analysis to be 63 % (1.3 D) at position 4 and 8 % (0.08 D) at position 5.

All solvents and piperylene were distilled before use. Commercial benzophenone and xanthone were employed as received.

Preparative photolysis of 2-isoxazolines.

Irradiation was carried out with a 10 W low-pressure mercury lamp (Vycor housing, mainly 253.7 nm) under bubbling nitrogen and external cooling with tap water. After removing the solvent under reduced pressure, the residue was separated by chromatography.

1. A solution of 1 (1.52 g) in 170 ml acetonitrile was irradiated for 24 hr and the photo-products were chromatographed on silica gel (50 g). Elution with 300 ml petroleum ether-benzene (2 : 1) afforded 125 mg of a yellow oil from which benzaldehyde and benzonitrile were isolated in 1.1 and 2.0% yields respectively, by vpc (20 % PEG-6000 on 40-50 mesh Celite 545; 140°; 1 atm/cm^2 gauge) and identified by IR. Further elution with 400 ml petroleum ether-benzene (1 : 1) followed by preparative tlc (30 : 1 petroleum ether-ethyl acetate) yielded 3 (150 mg; 15 %), mp 78-80°(lit[9] 85-86°) and recovered 1 (320 mg; 24 %).

Further elution with 300 ml benzene and then with 800 ml chloroform, followed by preparative tlc (15 : 1 petroleum ether-ethylacetate) gave 2 (190 mg; 19 %), mp 85.5-87° (lit[1] 82.5-83.3°), and 4[2] (45 mg; 3 %) as an oil, which showed satisfactory spectral and microanalytical data. From this eluate and the subsequent eluate with acetone, an intractable brown material (440 mg) was obtained. Styrene, identified by IR, was isolated by vpc (Silicone DC 550 (20 %) on 60-80 mesh Celite 545; 120°; 0.4 atm/cm^2) and the yield was estimated to be 1.6 % by vpc analysis of the photolysis mixture obtained by the irradiation of 1 under the same conditions followed by removing most of the solvent carefully through a Vigreux column.

5. A solution of 5 (2.23 g) in 220 ml acetonitrile was irradiated for 24 hr. The photolysis products were chromatographed on silica gel (70 g). Elution with 350 ml petroleum ether-benzene (2 : 1) followed by preparative tlc (petroleum ether) afforded cis-stilbene (230 mg; 33 %) and trans-stilbene (230 mg; 33 %), identified by IR. Elution with 200 ml petroleum ether-benzene (1 : 1) gave a yellow oil (90 mg) which was found to contain benzaldehyde (1.0 % yield) by vpc. Further elution with 1000 ml the same solvent mixture and then with 200 ml benzene yielded 5 (1.305 g; 59 % recovery). Successive elution with chloroform and acetone gave an intractable brown material.

5 (in the presence of cyclopentene).

A solution of 5 (1.6 g) and cyclopentene (20 ml) in 200 ml ether was irradiated in the same manner, followed by separating the products by cc and tlc (chloroform) to give 3-methyl-4,5-trimethylene-2-isoxazoline[3] (110 mg; 29 %), which was identical with an authentic sample[3] (IR), in addition to ca. 1 : 1 mixture of cis- and trans-stilbenes (260 mg; 47 %) and 5 (860 mg; 54 % recovery).

6. A solution of 6 (2.17 g) in 220 ml acetonitrile was irradiated for 25 hr and the products were separated by cc on silica gel (70 g). Elution with 600 ml petroleum ether-benzene (4 :1) followed by preparative tlc (petroleum ether) gave cis-stilbene (220 mg; 26 %) and trans-stilbene (110 mg; 13 %). Further elution with 250 ml benzene

gave a yellow oil (65 mg) which was found by vpc to contain benzaldehyde (0.7 % yield) and benzonitrile (0.6 % yield). Further elution with 800 ml benzene and then with 200 ml chloroform afforded 6 (620 mg; 31 % recovery). Further elution with 1000 ml chloroform followed by preparative tlc (benzene) yielded trans-7[4] (150 mg; 11 %), mp 99-109.5° (lit[4] 107-108°) and cis-7[4] as an oil (240 mg; 17 %; lit[4] mp 30-31°), the IR spectra of which were identical with those of authentic samples.[4] Further elution with chloroform and acetone gave an intractable material (290 mg).

8. A solution of 8 (0.80 g) in 100 ml acetonitrile was irradiated for 24 hr. The crude product mixture was crystallized from ca. 1 : 1 benzene-petroleum ether to give 10[28] (580 mg), mp 131-133° (lit[28] 127°), the spectral data of which were in accordance with those described in the literature.[28] The residue from the mother liquor was chromatographed on silica gel (10 g). Elution with 70 ml benzene afforded a trace of 8 identified by tlc. Further elution with 100 ml benzene gave 2,4-diphenyl-3-oxazoline 9 (51 mg; 6 %) as colorless crystals from benzene-petroleum ether, mp 100.5-101.5°. The structure of 9 was assigned from the spectral properties analogous to those of 2. IR(nujol) 1625 (C=N), 1060 and 1055 (C-O) cm^{-1} ; λ_{max}(EtOH) 246 (ε 17000) and 288 (sh, ε 490) nm; m/e 223 (M^+, rel. int. 100), 193 (M^+-CH_2O, 47) and 120 (M^+-PhCN,86); NMR($CDCl_3$) τ 2.00-2.74(m, 10H, arom) and a ABX signal at 3.12, 4.67 and 4.94 (3H, J_{AB}=15 Hz, J_{AX}=5 Hz, J_{BX}=4-5 Hz). (Found : C, 80.39; H, 5.79; N, 6.02 %. $C_{15}H_{13}NO$ requires : C, 80.69; H, 5.87; N, 6.27 %). Further elution with 400 ml 1 : 1 benzene-chloroform afforded 10 (110 mg; total yield 86 %). Even a trace of 2 was not detected in these fractions. On hydrolysis with hydrochloric acid 10 gave desoxybenzoin (94 %), mp 56-57°, as dexcribed in the literature.[28]

11. A solution of 11 (2.17 g) in 220 ml acetonitrile was irradiated for 29 hr. The photolysis product mixture was chromatographed on silica gel (80 g). Elution with 500 ml petroleum ether-benzene (2 :1) afforded acenaphthylene (190 mg; 57 %), identified by IR. Further elution with 400 ml benzene followed by preparative tlc (benzene) yielded a reddish yellow solid (50 mg; 2 %), which was recrystallized from

benzene-petroleum ether(1 : 1) to give yellow crystals, mp 122-123.5°. Structure 12 was tentatively assigned from the spectral properties : IR (nujol) 3200 (OH), 960 (N-O), 845 and 775 cm^{-1} (aromatic ring); NMR($CDCl_3$) τ 1.72 (1H, dd, J=6 and 1 Hz), 2.08-2.68 (6H, m), ca. 2.0 (1H, broad, disappeared by D_2O, O<u>H</u>), 7.65 (3H, s, C<u>H</u>$_3$); λ_{max}(EtOH) 406 (ε 2040) and 332 (ε 13000) nm; m/e 209 (M^+, rel. int. 32), 193 (61), 178 (100), 117 (76). (Found : C, 80.26; H, 5.37; N, 6.72 %. $C_{14}H_{11}NO$ requires : C, 80.36; H, 5.30; N, 6.69 %). Further elution with 900 ml benzene and then with 800 ml 1 : 5 chloroform-benzene gave 11 (1.72 g; 79 % recovery). Further successive elution with chloroform and acetone gave an intractable brown material (220 mg). The yield of 12 did not increase by prolonged irradiation and 12 was not transformed into acenaphthylene by photolysis at 253.7 nm.

Similar photolysis of 11 in the presence of cyclopentene in 200 ml of ether followed by the chromatographic separation of products yielded acenaphthylene and 12 in similar yields, but no 3-methyl-4,5-trimethylene-2-isoxazoline could be detected.

13. A solution of 13 (3.01 g) in 240 ml acetonitrile was irradiated for 62 hr and the photo-products were separated by silica gel (120 g) chromatography. Elution with 400 ml petroleum ether-benzene (1 : 1) gave 1-vinylnaphthalene (130 mg; 16 %) identified by IR. Further elution with 700 ml benzene followed by preparative tlc (3 : 1 petroleum ether-benzene or 15 : 1 : 0.2 petroleum ether-ethylacetate-acetic acid) gave α-naphthaldehyde (105 mg; 12 %) identified by IR, 13 (1.46 g; 49 % recovery) and an unknown substance (45 mg). This unknown substance (45 mg). This unknown substance was found not to be 2-phenyl-5,6-benzoquinolone[29] judging from its NMR and UV spectra. Finally, successive elution with benzene and chloroform yielded an intractable material (740 mg).

IR spectral monitoring of the photoreaction of 1.

Photolysis of 1 was carried out in the same manner as described above. Aliquots taken from the photolysate after 3, 6, 9 and 24 hr irradiation, respectively, were concentrated under reduced pressure and submitted to IR analysis (in acetonitrile). None of them showed an

absorption at 1745 cm^{-1} which is assignable to the C=N bond of 2-phenylazirine.[30]

Preparation of 2 from 2-phenylazirine and benzaldehyde.

A quartz tube containing a solution of 2-phenylazirine[30] (138 mg) and benzaldehyde (115 mg) in 10 ml acetonitrile was stoppered after flushing nitrogen and irradiated externally with a 10 W low-pressure mercury lamp with Vycor housing for 24 hr. Evaporation of the solvent followed by preparative tlc (chloroform) of the residue yielded 2 (28 mg; 23 % based on benzaldehyde) in addition to the recovered 2-phenylazirine (48 mg) and benzaldehyde (56 mg). Irradiation of a solution of 1 in acetonitrile under similar conditions yielded a trace of 2 identified by tlc and IR. Similar irradiation of a solution of equimolar amounts of styrene oxide and benzonitrile in acetonitrile did not give 2 at all.

Photolysis of 1 in the presence of acrylonitrile.

A solution of 1 (2.00 g) and acrylonitrile (50 ml) in 180 ml acetonitrile was irradiated with a 10 W low-pressure mercury lamp for 48 hr. Chromatographic separation of the product mixture on silica gel (80 g) afforded recovered 1 (350 mg) benzaldehyde (45 mg), benzonitrile (55 mg), 2-phenylquinoline (3; 200 mg), and β-aminochalcone (4; 60 mg). The chromatographic column was finally eluted with chloroform to give 2-phenyl-4-cyano-Δ^1-pyrroline (550 mg), being purified by preparative tlc (3 : 1 benzene-ethyl acetate) followed by crystallization from carbon tetrachloride-acetone, mp 100-102° (lit[5] 95-96°). The NMR, IR and mass spectra were in accordance with those reported.[5]

Photolysis of 2 in the presence of acrylonitrile.

As a control experiment, a solution of 2 (410 mg) in acetonitrile (70 ml) was irradiated for 96 hr. as above. After evaporation of the solvent, the residue was submitted to preparative tlc (chloroform) to give benzoic acid (35 mg), 2 (35 mg) and phenanthro [9,10-d]oxazole (15 mg), mp 147-153° (from aqueous methanol) (lit[31] 152°), which was identical with an authentic sample[31](IR). Even a trace of 1 could not be detected.

Similar irradiation of a solution of 2 (280 mg) and acrylonitrile (20 ml) in 90 ml acetonitrile for 46 hr followed by the separation of the product mixture by preparative tlc (5 : 1 benzene-ethyl acetate) gave the recovered 2 (185 mg) and 2-phenyl-4-cyano-Δ^1-pyrroline (30 mg).

Photolysis of 1-d.

A solution of 1-d (0.74 g) in 150 ml acetonitrile was irradiated for 13.5 hr under the same conditions as described in the photolysis of 1. After similar work up of the photolysate, 3-d (79 mg; 11 %), mp 85-87.5°, 2-d (93 mg; 13 %), mp 85.5-86.5°, unlabeled benzaldehyde (4 mg; 1.1 %) and the recovered 1-d (59 mg; 8 %) were obtained. The position and content of deuterium in these compounds were determined by NMR and mass spectroscopic analyses as follows. NMR(CCl_4): 2-d : 62 % (1.2 D) at position 2; 7 % (0.07 D) at position 5. 3-d : signal intensity at τ 2.25 (1H, d, J=8.5 Hz) of 3 descreased over 90 %. Recovered 1-d : 63 % (1.3 D) at position 4; 7 % (0.07 D) at position 5. Benzaldehyde : less than 16 % (0.16 D) in CHO proton. Mass : 2-d : 224 (M^+, relative intensity 0.2), 121 (M-PhCN, 100), 118 (M-PhCHO, 40), 117 (12). [2; 223 (M^+, 0.3), 120 (M-PhCN, 100), 117 (M-PhCHO, 61).] The data show that most of D of 2-d is present at position 2.

2-Nitrochalcone-α-d.

(i) According to the method[10] for the monodeuteration of chalcone, 2-nitrochalcone (425 mg)[9] in 40 ml anhydrous ether was mixed with a solution of sodium (11 mg) dissolved in 10 ml methanol under cooling with ice water and the mixture was stirred for 48 hr. A small amount of solid precipitated was removed by filtration from the mixture, and the filtrate was evaporated under reduced pressure. The residue was taken up in 40 ml chloroform and the chloroform solution was washed quickly with 20 ml cold water and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure left a brown solid, which was crystallized from ethanol to give 2-nitrochalcone-α-d (245 mg; 58 %), mp 124-125 ° (lit mp of undeuterated 2-nitrochalcone, 122-123°[9]). The NMR showed complete disappearance of a doublet signal (τ 2.66, J=15 Hz) of undeuterated 2-nitrochalcone and broadening another doublet (τ 1.80,

J=15 Hz).

(ii) According to the method[11] for the condensation of benzaldehyde with acetophenone-2,2,2-d_3, a solution of o-nitrobenzaldehyde (1.18 g) and acetophenone-2,2,2-d_3[12] (1.10 g) in 10 ml MeOD was treated with 1.8 ml 40 % NaOD in D_2O and 5.2 ml D_2O under cooling with ice water for 3 hr. After a solid material was removed by filtration and washed with 20 ml ethanol, the combined filtrates were evaporated under reduced pressure to give a brown solid (255 mg), which was submitted to preparative tlc (5:1 benzene-chloroform) followed by crystallization from ethanol to give the titled compound (7 mg; 0.5 %). The IR spectrum was identical with that of the sample obtained above.

2-Phenylquinoline-3-d (3-d).

2-Nitrochalcone-α-d (52 mg) was converted into 3-d according to the method by Fèrve and Pearson,[9] with omitting the procedure for the isolation of 3-d hydrochloride. Thus, the reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was triturated with 6 ml ca. 2.5 % aqueous ammonia and collected by filtration. The residue dissolved in 10 ml ethanol was filtered again and evaporated to give a brown solid (44 mg), which was purified by preparative tlc (benzene) to afford 3-d (18 mg) as a colorless solid. The IR and NMR spectra were identical with those of 3-d obtained by the photolysis of 1-d.

Photolysis of 2-isoxazolines 6,8 and 13 under various conditions (Table 2).

Irradiation was done under the given conditions, either internally or externally. External irradiation was carried out in a Pyrex tube (light source B and C) or a quartz tube (A), which was stoppered after bubbling nitrogen through a sample solution. Products were isolated by cc and/or preparative tlc and identified by spectroscopic and tlc techniques.

Experiment No. 9 (Table 2) was performed as follows. A solution of 6 (1.02 g) in 350 ml acetonitrile was irradiated under air with occasionally shaking. The product mixture was submitted to cc (silica

gel, 40 g). Elution with 400 ml petroleum ether-benzene (1 : 1) gave an oil (12 mg) which was found by tlc and IR to contain a trace of benzonitrile. Successive elution with 300 ml of the same solvent mixture, 1000 ml benzene and 200 ml chloroform, followed by preparative tlc (1 : 10 petroleum ether-benzene) yielded tribenzamide (325 mg; 29 %), mp 216-218 ° (lit[32] 208°) and benzoic acid (155 mg; 12 %), identified by IR. Further elution with 200 ml chloroform-acetone (10 : 1) followed by preparative tlc (50 : 1 chloroform-acetone) afforded dibenzamide (55 mg; 7 %), mp 149.5-151 ° (lit[33] 147°). Further elution with the same solvent mixture and then with acetone gave an intractable material (300 mg) which was not further examined.

Acknowledgement

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C H A P T E R III

Photochemical cis-trans Isomerization of 2,4,5-Triphenylimidazoline

Irradiation of cis-(amarine, I) and trans-(isoamarine, II) 2,4,5-triphenylimidazolines in acetonitrile or benzene gave a photostationary mixture of cis- and trans- isomers, the latter predominating over the former. On irradiation in a dilute acetone solution under the conditions that acetone absorbed most of the light, cis-trans isomerization occurred only with isoamarine but not with amarine. In acetone, 2,4,5-triphenylimidazole(III) was also formed. Two kinds of intermediate species for the cis-trans isomerization were proposed : imidazolinyl radical(IV or V) (in acetone) and biradical or zwitterionic species (VIa) (in acetonitrile or benzene). Evidences for the intermediacy of VIa are presented.

1. Introduction

It will be shown in the next chapter[1] that imidazolines, on irradiation in acetone solutions, are dehydrogenated to give the corresponding imidazoles *via* imidazolinyl radicals which are formed by hydrogen abstraction with excited acetone. In the course of this investigation 2,4,5-triphenylimidazolines, amarine(I; *cis*) and isoamarine(II; *trans*) were found to undergo cis-trans isomerization simultaneously with dehydrogenation to 2,4,5-triphenylimidazole(III; lophine). Since such a type of cis-trans isomerization in heterocyclic systems appeared relatively rare,[2] the photochemical cis-trans isomerization of I and II was examined in some details.

2. Results and Discussion

Cis-trans isomerization of I and II under various conditions.

Amarine(I) and isoamarine(II) were irradiated with a 100 W high-pressure mercury lamp (Pyrex) or a 10 W low-pressure mercury lamp (Vycor, mainly 2537 Å) under bubbling nitrogen in various solvents at different concentrations. The results are summarized in Table 1. The material balance of the photoreaction induced by a Pyrex-filtered light was considerably good, and products other than I, II and lophine(III) were obtained only in small yields (vide infra).

In acetonitrile, no lophine(III) was formed and a photostation-

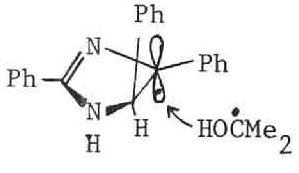
ary mixture of I and II with predominance of the thermodynamically more stable isomer II was obtained from either I or II. Piperylene, a triplet quencher, failed to quench the cis-trans isomerization at various concentration (Table 2), indicating that the excited state responsible for the isomerization may be singlet or short-lived triplet.

In benzene, which is known as a triplet sensitiger except a few exceptional cases,[3] only a trace of III was detected and the photostationary mixture of I and II was obtained in the similar ratio to that in acetonitrile. Both I and II were found to isomerize at such a low concentration (0.17×10^{-2} M) that more than 99 % of the incident light was absorbed by benzene. It was also found that the II/I ratio in the isomerization of I in benzene decreased with increase of the amount of added piperylene (Table 3), possibly due to partial quenching of the benzene triplet. These results suggest that the cis-trans isomerization of I and II may take place at least partly from their short-lived triplet state.

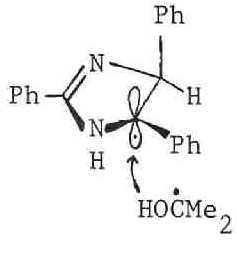
In acetone lophine(III) was always formed to a considerable extent regardless of the light sources , and the cis-trans isomerization was found to be dependent on the initial concentration of I and II. At low concentrations (ca. 3×10^{-4}M), at which more than 99 % of the incident light was absorbed by acetone, the isomerization occurred only from isoamarine(II) toward amarine(I) but not from I toward II. At high concentrations (ca. 3.5×10^{-2}M), at which about 50 % of the incident light was absorbed by acetone, either I or II afforded a photostationary mixture of I and II with predominance of I over II in con-

trast to the case in acetonitrile and in benzene. These results obviously indicate that the mechanism of the cis-trans isomerization in acetone solution is different from that in acetonitrile or benzene solution.

In the next chapter, it will be described that excited acetone can abstract a hydrogen atom at 4- or 5- position of imidazolines to yield a imidazolinyl radical and a acetone ketyl radical, and that the resultant imidazolinyl radical can be led either to the original imidazoline, a hydrogen atom being provided by the acetone ketyl radical, or to the corresponding imidazole. It is, therefore, quite reasonable to suppose that the photochemical cis-trans isomerization of I and II in dilute acetone solutions accompanied with dehydrogenation of both I and II to III proceeds through the imidazolinyl radicals IV and/or V as depicted in Scheme 1(A). The completely stereoselective isomerization toward I in dilute acetone solutions must require that the hydrogen transfer from the acetone ketyl radical to the imidazolinyl radicals IV and/or V occurs only in the direction toward the thermodynamically less stable isomer I but not toward II.[4] The acetone ketyl radical may attack IV and/or V predominantly from the opposite side of a bulky phenyl group as shown below. At high concentrations of I and II in acetone, cis-trans isomerization from their excited



IV

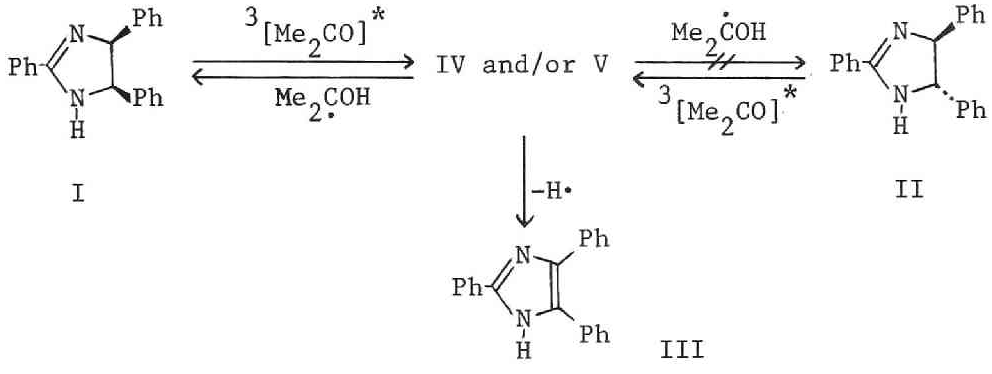


V

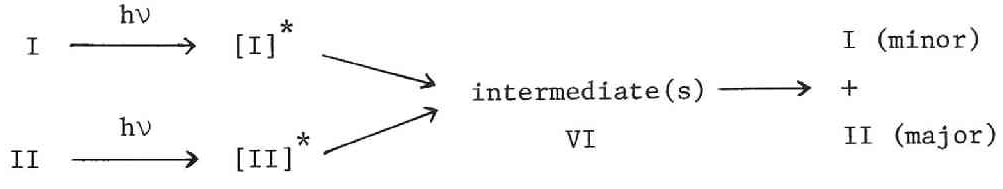
state as in acetonitrile or benzene [Scheme 1 (B)] is possibly competing with cis-trans isomerization via the imidazolinyl radicals. Thus, it is reasonably explained that the II/I ratio obtained at higher concentrations in acetone is smaller than that obtained in acetonitrile or benzene. It should be noticed that these two processes shown in Scheme 1 provide a typical example of kinetically (A) and thermodynamically (B) controlled cis-trans isomerizations.

Scheme 1.

A [in dilute acetone solutions]



B [in acetonitrile or benzene]



Irradiation of I in isopropyl alcohol or ether under the similar conditions also resulted in the cis-trans isomerization with predominance of II over I.

Table 1. Photochemical cis-trans isomerization of amarine and isoamarine in various solvents.

Solvent	Starting material	Concn. ($\times 10^{-2}$M)	Light source[a]	Irradn. time(hr)	II/I ratio	Yield(%) III	Yield(%) I+II
MeCN	I	3.14	B	24	1.8	0	61
	II	3.12	B	24	1.6	0	63
	I	1.77	A	8	2.3	0	96
	II	1.71	A	8	2.3	0	93
C_6H_6	I	3.45	A	15	1.6	trace	96
	I	0.172	B	3	1.6	trace	n.d.[b]
	II	0.168	B	3	1.4	trace	n.d.
Me_2CO	I	3.55	B	24	0.60	35	41
	I	3.27	A	15	0.46	21	74
	I	0.0282	A	1	0	29[c]	n.d.
	II	3.62	B	24	0.59	28	43
	II	0.0302	A	1	~0[d]	19[c]	n.d.
Me_2CHOH	I	3.54	A	15	3.0	0	95
Et_2O	I	1.36	A	15	1.8	trace	n.d.

a) A : high-pressure mercury lamp (Pyrex)
B : low-pressure mercury lamp (2537 Å)

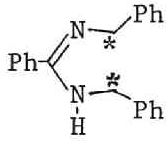
b) not determined

c) determined after 30 min irradiation

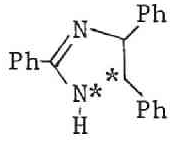
d) II/I ratio is 0.43 after 0.5 hr, 0.083 after 1 hr.

What is the intermediate VI ?

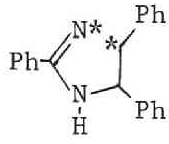
It seems reasonable to assume a homolytic or a heterolytic bond cleavage of ring bonds (VIa, VIb, VIc or VId) as an intermediate step of cis-trans isomerization in acetonitrile or benzene. An alternative pathway involving migration of hydrogen (VIe or VIf) is also a possible



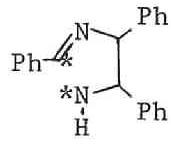
VIa



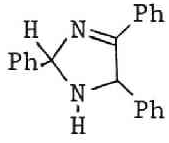
VIb



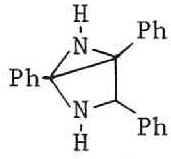
VIc



VId



VIe



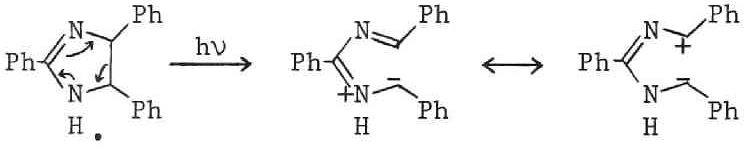
VIf[5]

* = •, + or -

one although less probable because of the following difficulties. If 1,3-hydrogen shift occurs stepwise and homolytically in the process I (or II) $\underset{h\nu}{\overset{h\nu}{\rightleftharpoons}}$ VIe, the imidazolinyl radical IV must be transiently formed and consequently lophine(III) must be formed concurrently. Since III was unable to be detected among products at least in acetonitrile, the 1,3-hydrogen shift should proceed concertedly and suprafacially[6] and should result in no cis-trans isomerization by the intermediacy of VIe. The intermediate VIf also has the difficulty in explaining the results that deuterium incorporation is very ineffective by irradiation of I in acetonitrile-D_2O (below 1.9 % after above half of I isomerized into II).

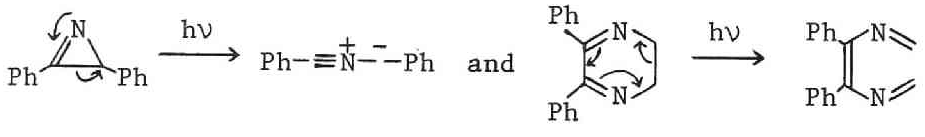
Among possible biradical or zwitterionic intermediates(VIa - VId), VIa is the most plausible one in view of bond dissociation energy data

for similar types of bonds : $PhCH_2$-CH_2Ph (45-48 kcal/mol)[7] and $PhCH_2$-$NHCH_3$ (58 kcal/mol).[8] The bond dissociation energy data for C=N-C and N-C=N bond are not available, but they may have a higher value than the others considering the less resonance-stabilized nature of C=N· or ·C=N radical. The photochemical homolytic cleavage of C-C bonds has been recently reported.[2,9] Furthermore, the heterolytic cleavage to generate VIa has some analogy to that of azirines[10] and 2,3-dihydropyrazines.[11]



VIa

Compare with

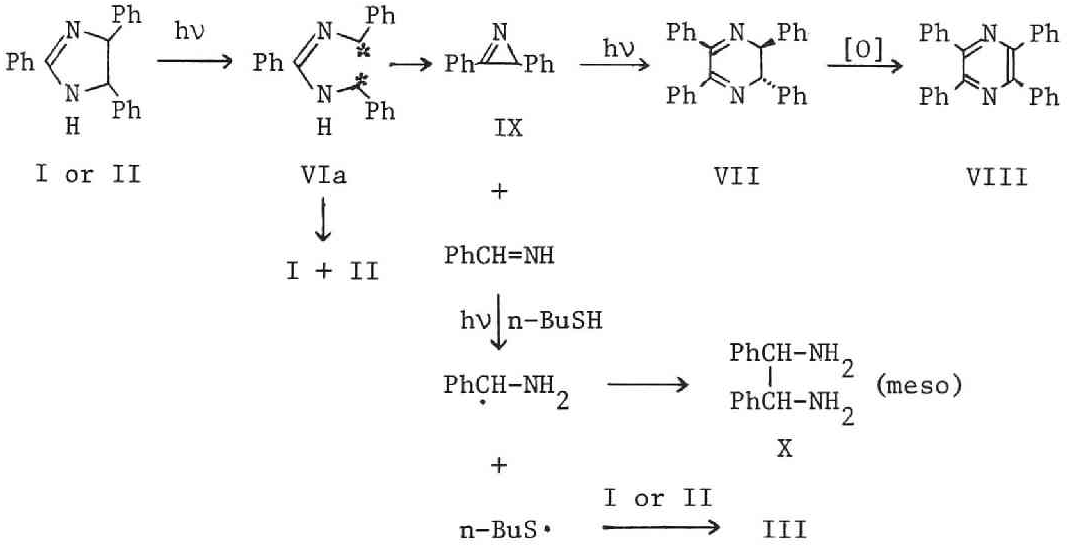


In order to know whether the rupture of C_4-C_5 bond of I or II (VIa) occurs, it was attempted to isolate byproducts which may be formed from the plausible intermediate VIa. And, it was also attempted to trap the intermediate VIa by radical scavengers such as n-butyl mercaptan,[12] oxygen and 2,2,6,6-tetramethylpiperidine-1-oxyl[13] and by the solvent isopropyl alcohol.[9a]

Amarine(I) in acetonitrile was irradiated with light through Pyrex and trans-2,3,5,6-tetraphenyl-2,3-dihydropyrazine(VII, 2 %) was isolated by chromatographic procedures. In addition, 2,3,5,6-tetraphenylpyrazine(VIII), which was probably formed during work-up by autoxida-

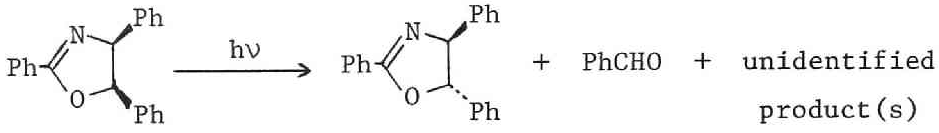
tion of VII[14b] was detected on tlc. In spite of the same irradiation conditions as in Table I, a small amount (1-2 %) of lophine(III) was formed in this case. Since it is already known that VII and VIII are formed photochemically from 2,3-diphenyl-2H-azirine(IX)[14], the intermediacy of IX in the transformation of I into VII can be assumed. The cis-trans isomerization of I and the formation of IX can be well interpreted by considering a common intermediate VIa as shown in Scheme 2. The double cleavage similar to that of I or II leading to IX was also observed in the photoreaction of 2-isoxazolines[15] (type iv [2 + 2] reaction in the notation used in Chapter I of Part I.

Scheme 2.



It is worthwhile to mention about the preliminary results of photolysis of cis-2,4,5-triphenyloxazoline(XI). Upon photolysis (2537 Å) XI afforded its trans-isomer (14 %) and benzaldehyde, but the main product or products were not identified. It should be noticed that this re-

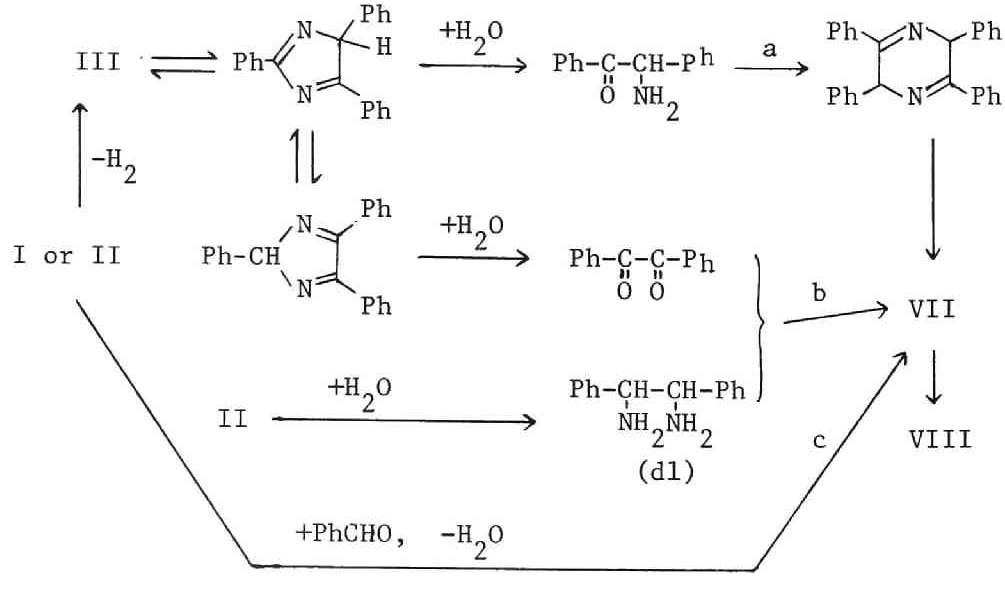
action is also explained by cleavage of the C_4-C_5 bond as the first step. If the O_1-C_2 bond is first broken, benzonitrile must be formed considering the photofragmentation of 2-isoxazolines.[15]



cis-XI trans-XI

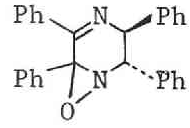
The formation of VII may be rationalized by other mechanisms (Scheme 3). The pathways a and b were eliminated by the fact that photolysis of lophine(III) or a mixture of III and dl-stilbenediamine didn't yield even a trace of VII and VIII. The pathway c, which must involve complex reactions, was ruled out, because the photolysis of I in acetonitrile in the presence of a small amount of benzaldehyde added externally resulted in the decrease of yields of VII and VIII.

Scheme 3



In fact, only <1 % yields of VII and VIII along with a new product,

which was assigned as oxaziridine XII (2 % yield) on the basis of spectral data and an indepenent synthesis, were isolated in addition to I and II.

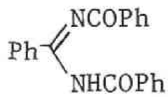


XII

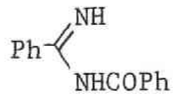
Attempts for trapping of VIa with n-butyl mercaptan (0.38 M in acetonitrile), 2,2,6,6-tetramethylpiperidine-1-oxyl (0.127 M in benzene) and the solvent isopropyl alcohol were unsuccessful. However, from the result obtained with n-butyl mercaptan some information supporting Scheme 2 was obtained. Thus, irradiation (Pyrex) of I in acetonitrile in the presence of n-butyl mercaptan afforded VII (2 %), VIII (3 %), III (48 %), I (17 %), II (9 %) and meso-stilbenediamine (X, 2 %). The last compound appears to be a product derived from benzaldimine, the counterpart of IX (Scheme 2). Photochemical reductive dimerization of imines with suitable hydrogen donor is well-known.[16] The formation of a large amount of III may be attributed at least partly to hydrogen abstraction with the n-butane thiyl radical.[17]

Irradiation (Pyrex) of I in acetonitrile under bubbling oxygen gave N,N'-dibenzoylbenzamid-ine (XIII, 43 %), N-benzoylbenzamidine(XIV), dibenzamide(XV) (the total yield of XIV and XV is 16 %) and II (13 %). At first glance, the oxidation of I to XIII appeared that the intermediate VIa was trapped by oxygen. There are, however, reports[18,19] that the photochemical oxidation of III produces lophine hydroperoxide(XVI), which decomposes gradually to XIII. In the present photooxidation of I, neither III nor XVI could be detected (tlc). But, at low temperature (-78°) at which the intermediate XVI is stable and accumulates as the primary photooxidation product of III,[18] I resisted to photooxidation and only underwent cis-trans

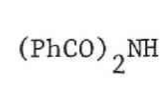
isomerization. Therefore, it could not be unambiguously determined whether XIII - XV were formed via VIa.



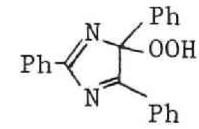
XIII



XIV



XV



XVI

In conclusion, the cis-trans isomerization of I and II, the bond energy data, the isolation of VII and X, and the photoproducts of XI are well accommodated by a mechanism involving the scission of C_4-C_5 bond. The result of photochemical oxidation of I is not inconsistent with this mechanism.

3. Experimental

All the melting points are uncorrected. NMR spectra were taken on a NEVA T-60 spectrometer with tetramethylsilane as the internal standard. IR and UV spectra were measured on a JASCO IRS spectrophotometer, and on a MODEL ORD/UV-5 Japan Spectrometer, respectively. Column chromatography was carried out with Mallinckrodt silica gel (100 mesh) as the adsorber. Thin layer chromatography (tlc) was carried out with Merck Kieselgel GF_{254} using uv light and iodine for compound detection.

Synthesis of amarine(I) and isoamarine(II) will be described in the next chapter. All the solvents were distilled before use.

Cis-trans isomerization of I and II under various conditions (Table 1).

As described in Table 1, a solution of I or II dissolved in a solvent, 110 ml when a 100-W high-pressure mercury lamp (Pyrex filter) was used, 220 ml when a 10-W low-pressure mercury lamp (Vycor filter, mainly 2537 Å) was used, and 500 ml (acetone) for low concentration experiments, was irradiated several hours under bubbling nitrogen.

After evaporation of the solvent under reduced pressure, the residue was subjected to NMR analysis (CCl_4-DMSO-d_6) and the II/I ratio was determined from the peak intensities of singlets at τ 4.55 for I and τ 5.10 for II. The yields of lophine(III) and recovered imidazolines (I + II) were determined by UV analysis (EtOH) and NMR analysis (CCl_4 + DMSO-d_6; pinacol or 2-methylimidazoline as the internal standard), respectively. In solvents except acetone, none or a trace of III was detected by careful tlc analysis.

Quenching of the cis-trans isomerization of I.

Pyrex tubes (volume 20 ml) containing a fixed amount of I and freshly distilled piperylene (45-47 °C) in acetonitrile were sealed after bubbling nitrogen through the solution and irradiated externally on a merry-go-round apparatus. After removing the solvent and the piperylene under reduced pressure, the II/I ratio was determined by NMR technique (Table 2).

The results of Table 3 were obtained by irradiating a fixed amount of I and piperylene in benzene (220 ml) under bubbling nitrogen and by determining the $\frac{II}{I}$ ratio by NMR spectroscopy.

Isolation of byproducts and experiments to trap VIa in the cis-trans isomerization of I.

All irradiations were done with a 100-W high pressure mercury lamp(Pyrex filter) under bubbling nitrogen, unless otherwise specified. The photoproducts obtained after removing the solvent under reduced pressure were separated and characterized in the following way.

A) Isolation of byproducts.

The product mixture (after 17 hr irradiation)[20] from a solution of I (1.17 g) in acetonitrile (110 ml) was chromatographed on silica gel (40 g). Elution with 200 ml of 1 : 1 benzene-chloroform gave 12 mg of a solid which contained a trace of 2,3,5,6-tetraphenylpyrazine (VIII) (tlc). Further elution with 400 ml of the same solvent, followed by preparative tlc, afforded 35 mg (2 %) of VII (IR, NMR, tlc) and 15 mg (1-2 %) of III (IR, tlc). Further elution with the same solvent and finally with acetone gave 760 mg of II and 350 mg of I,

Table 2. Quenching of excited I with piperylene in acetonitrile[a]

Piperylene added(M)	0	0.0604	0.12	0.179	0.237	0.295	0.573
II/I ratio[b]	0.24	0.31	0.33	0.30	0.27	0.26	0.27

a) Initial concentration of I : 2.05×10^{-2} M, Light source, irradiation time and temperature : 450-W high pressure mercury lamp (Pyrex), 3 hrs and 30+1°C, respectively.

b) Irradiation of I without piperylene showed that the value of II/I ratio increased almost linearly with increased irradiation time in the earlier stage of photolysis.

Table 3. Quenching experiment with piperylene in benzene[a]

Initial concentrations[b] of I ($\times 10^3$ M)	1.71	1.87	1.72
Piperylene added(M)	0	0.0421	0.633
II/I ratio	1.6	1.4	0.8

a) Light source : 10-W low pressure mercury lamp (Vycor). Irradiation time : 3 hr

b) At these concentrations of I, more than 99 % of the incident light is absorbed by benzene.

respectively (total yield of I and II, 95 %).

B) Irradiation of I with trapping reagents.

i) n-Butyl mercaptan. A chloroform-unsoluble part of the product mixture (after 15 hr irradiation) from a mixture of I (2.33 g=0.035 M) and n-butyl mercaptan (9.0 ml=0.38 M) in acetonitrile (220 ml) was recrystallized from acetone and 135 mg of III was obtained. The residue from the mother liquor was chromatographed on silica gel (70 g). Elution with 700 ml of chloroform afforded a yellow solid, which after preparative tlc (benzene) yielded 60 mg (3 %) of 2,3,5,6-tetraphenylpyrazine(VIII) mp 260-261°C (acetone-chloroform) (Lit[21] 252°C) and 40 mg (2 %) of trans-2,3,5,6-tetraphenyl-2,3-dihydropyrazine(VII), mp 205-206°C (chloroform-ethanol) (Lit[22] 199.5-200.5°C). The spectral data of VII were identical with an authentic sample.[22] The IR spectrum of VIII was identical with that in the Sadtler Standard Spectra. Further elution with 800 ml of chloroform yielded 990 mg of III (total yield of III, 48 %). Further elution with chloroform and acetone, followed by preparative tlc (1 : 1 chloroform-acetone), yielded I (380 mg) and II (210 mg) and 40 mg (2 %) of meso-stilbenediamine(X), mp 121-123°C (ligroin-ether) (Lit[23] 118-120°C) which was identical with an authentic sample.[24]

ii) Oxygen. The product mixture obtained from photolysis (15 hr) of a solution of I (1.07 g) in acetonitrile (110 ml) under bubbling oxygen instead of nitrogen was separated by preparative tlc (30-50 : 1 chloroform-acetone). Following products, in the order of increasing R_f values, were isolated : (1) N,N'-Dibenzoylbenzamidine(XIII); 460 mg (43 %), which was unstable on silica gel (Kieselgel GF_{254}) or alumina (Aluminiumoxide GF_{254}) and decomposed to a mixture of XIII, XIV and XV as reported earlier[18,19] but could be obtained in a sufficiently pure state for IR and NMR measurements. Its identity was confirmed by comparison with an authentic sample.[19] (2) N-Benzoylbenzamidine (XIV) and (3) dibenzamide(XV); combined yield, 165 mg (16 %). These two compounds had the same R_f value of tlc ($CHCl_3$) and XIV decomposed on tlc to give XV. Recrystallization of the mixture from 3 : 1

ligroin-acetone, however, could yield pure XV, mp 152-154°C (Lit[25] 147-148°C) which was identified by NMR and IR spectra and had an UV spectrum identical to the published data.[26] The residue from the mother liquor consisted of mainly XIV, whose NMR and IR spectral data were in accord with those of an authentic sample.[19] (4) Isoamarine (II) ; 140 mg (13 %). Amarine(I) was not detected. The transformation of III to lophine hydroperoxide(XVI) at -78° was carried out according to the method of White and co-workers[18] using a 100-W mercury lamp (Pyrex) instead of a sunlamp. Low-temperature (-78°) oxidation of I was also carried out in the same manner and the reaction was followed by tlc, giving results that only I and II were detected, but III, XIII, XIV, XV and XVI could not be detected.

iii) 2,2,6,6-Tetramethylpiperidine-1-oxyl.[27] A mixture of I (1.14 g, 0.0191 M) and this free radical (3.96 g, 0.127 M) in benzene (200 ml) was irradiated under nitrogen with the 313 nm light isolated from a 100-W mercury lamp with a chromate-carbonate filter.[28] The reaction was followed by tlc confirming the occurrence of cis-trans isomerization. In addition, a small amount of III was detected.[29] However, products expected from the trapping of VIa by the nitroxyl radical could not be observed until 52 hr of irradiation . At this point an aliquot of the photolysate was submitted to preparative tlc (30 : 1 chloroform-ethanol) and an almost equal amount of I and II and a trace of III were isolated. The nitroxyl radical was fairly stable under these conditions and was largely recovered unchanged (ca. 72 %).

iv) Isopropyl alcohol. After 70 hr of irradiation, the photolysate from I (1.01 g) in isopropyl alcohol (100 ml) contained no significant product except I and II as the main product and traces of III, VII and VIII by tlc analyses.

Photolysis of I in the presence of benzaldehyde.

The mixture obtained by the photolysis (15 hr) of a solution containing 1.01 g (3.41×10^{-2} M) of I and 50 µl (4.81×10^{-3} M) of benzaldehyde in acetonitrile (110 ml) with a 100-W high pressure mercury lamp (Pyrex) under bubbling nitrogen was evaporated and the residue

was chromatographed on silica gel (30 g). Elution with chloroform, followed by preparative tlc (benzene or 20-50 : 1 chloroform-acetone) of the eluates, yielded 3 mg (< 0.5 %) of VIII, 5 mg (< 0.5 %) of VII, 20 mg (2 %) of III and 23 mg (2 %) of XII. Further elution with chloroform and acetone afforded 530 mg (52 %) of II and 435 mg (43 %) of I. The structure of XII, mp 184-185°C (petroleum ether-methanol), was assigned from its spectral and analytical data ; ν (film) 1665, 1325 cm^{-1} ; τ (CCl_4) 2.17-3.17 (20H, m, arom), 4.88(1H, d, J=3 Hz) and 4.98 (1H, d, J=3 Hz);λ_{max}(EtOH) 242 (ε 18400) nm. (Found : C, 83.48; H, 5.65; N, 6.82 %. Calcd for $C_{28}H_{22}N_2O$: C, 83.55; H, 5.51; N, 6.96 %).

Synthesis of XII.

To a solution of 90 mg (2.33×10^{-4} M) of VII in 1 ml of chloroform was added dropwise 450 mg (2.93×10^{-4} M) of perbenzoic acid (9 % chloroform solution) with stirring. The mixture was stirred for further 1 hour at room temperature, and evaporated to dryness. The residue was separated by preparative tlc (chloroform) and 15 mg (23 %) of XII was isolated as the main product which showed an IR spectrum identical with that of XII obtained photochemically. The method to prepare oxaziridines by the action of peracids or aerated aldehydes on Schiff's bases is well-known.[30]

Photolysis of III in the presence or absence of dl-stilbendiamine.

Two Pyrex tubes containing each a solution of III (10 mg) in acetonitrile (20 ml) and a solution of III (11 mg) and dl-stilbenediamine (5 mg) in acetonitrile (20 ml) were irradiated externally with a 400-W high pressure mercury lamp (Pyrex) under bubbling nitrogen for 8 hours. By careful examination of the photolysate by tlc VII and VIII were not detected at all.

Deuterium incorporation experiment.

A solution of 94 mg of I in a mixture of acetonitrile (15 ml) and D_2O (5 ml) placed in a Pyrex tube was sealed after bubbling nitrogen and irradiated externally with a 450-W high pressure mercury lamp for 16 hr. After evaporation of the photolysate under reduced

pressure, the residue (II/I = 1.2 by NMR) was dissolved in chloroform (20 ml) and washed four times with 20 ml of water to remove deuterium bound to nitrogen. The solution was evaporated after drying over Na_2SO_4 and was separated by preparative tlc (3 : 2 chloroform-acetone) to give I (25 mg) and II (34 mg). The latter was recrystallized from ether-ethanol and analyzed by mass spectroscopy (HITACHI RMU-6C) to determine deuterium content. It was estimated as less than 1.9 % from comparison with the mass spectrum of the non-deuterated II.

Photolysis of cis-2,4,5-triphenyloxazoline (XI).[31]

A solution of XI (1.03 g) in acetonitrile (220 ml) was irradiated with a 10-W low pressure mercury lamp (Vycor) under bubbling nitrogen for 15 hr. After removing the solvent under reduced pressure, the residue (1.03 g) was chromatographed on silica gel (50 g). Elution with benzene (400 ml) afforded 35 mg of a yellow oil which contained ca. 1 mg of benzaldehyde (IR) by vpc analysis. Further elution with benzene (400 ml), followed by preparative tlc (2 : 1 chloroform-benzene), afforded 144 mg of trans-2,4,5-triphenyloxazoline ; mp 86-87.5° (from petroleum ether) (lit[31] 83-85°), which gave satisfactory spectral and analytical data. Further elution with benzene (1.6 l), followed by preparative tlc (5 : 1 chloroform-benzene), afforded a white solid (345 mg) ; mp 122-135° (from petroleum ether-acetone), which was unidentified.

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C H A P T E R IV

Photochemical Dehydrogenation of Imidazolines to Imidazoles

Imidazolines were found to be dehydrogenated to imidazoles by irradiation with light at 2537 Å or above 2900 Å in acetone. The n, π^* triplet acetone acts as hydrogen abstracting agent giving 4- and/or 5-imidazolinyl radicals which in turn are transformed into imidazoles. This scheme is supported by the facts that the AIBN-initiated dehydrogenation of imidazolines gave corresponding imidazoles, that oxygen quenched the photochemical dehydrogenation, and that in some cases coupling products between the imidazolinyl and the acetone ketyl radicals were formed. Various data indicate that the imidazolinyl radical reverts back to the parent imidazoline by hydrogen transfer from the acetone ketyl radical during photolysis.

1. Introduction

There are several reports on the methods for dehydrogenation of imidazolines leading to corresponding imidazoles.[1] These methods involve dehydrogenation with catalysts such as nickel, iron, platinum and palladium or with hydrogen acceptors such as sulfur and selenium. It is well known that a variety of carbonyl compounds, in their excited states, can abstract hydrogen from various hydrogen-donating substrates.[2] However, examples of the photochemical dehydrogenation of hydroaromatic compounds to aromatic compounds are relatively few,[3] since simple carbonyl compounds often photochemically react with a hydrogen donor to form coupling products.[6] In the present chapter the author report a simple method for dehydrogenating imidazolines to imidazoles by irradiation in acetone.

2. Results

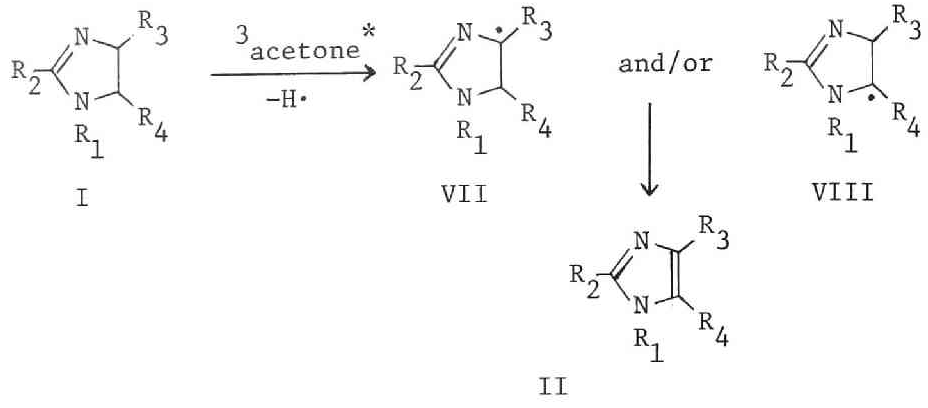
Irradiation of an acetone solution of imidazolines(I) with a low-pressure mercury lamp (mainly 2537 Å) under nitrogen followed by column chromatography of the reaction products gave corresponding imidazoles (II) in reasonable yields. The results are summarized in Table 1. 2-Methylimidazolines(Ia and Ib) gave dehydro-coupling products (III, IV and V) besides corresponding imidazoles, but 2-hydroxyimidazoline (Ii) only a coupling product VI. It should be noted that both cis-

(If; amarine) and trans- (Ig; isoamarine) 2,4,5-triphenylimidazolines underwent cis, trans-isomerization being accompanied with dehydrogenation to 2,4,5-triphenylimidazole(IIf; lophine). Acetone pinacol was isolated in low yield only in cases of Ia and Ib but not detected in all other cases.

Oxygen was found to quench the formation of an imidazole. Thus, irradiation of 2-methylimidazoline(Ia) under similar conditions except under bubbling oxygen instead of nitrogen gave no 2-methylimidazole(IIa) but 2-methylimidazolinium acetate (12 %) besides some recovered starting material (27 %). Irradiation of an acetone solution of Ia, which had been degassed by four freeze-thaw cycles at 10^{-4} mm under cooling with liquid nitrogen, gave no effect on the reaction, and the IIa, IIIa and pinacol were obtained in the same ratio as that under nitrogen. On irradiation in benzene or isopropyl alcohol under nitrogen, these imidazolines (Ib, Ic, Id and Ie) were recovered unchanged except that cis, trans-isomerization was observed with amarine(If) and isoamarine (Ig).[7] Therefore it is considered that the imidazoles were formed via 4-(VII) and/or 5-(VIII) imidazolinyl radicals which were formed from the imidazolines by hydrogen abstraction with the n, π^* triplet state of acetone as shown in Scheme 1.

In order to ascertain this scheme, hydrogen abstraction of 2-methylimidazoline(Ia), amarine(If) and isoamarine(Ig) by the 1-cyano-1-methylethyl radical generated by thermolysis of azobisisobutyronitrile(AIBN) was carried out. As shown in Table 2, corresponding imidazoles were obtained and the yields of the imidazoles were dependent

Scheme 1.



I VII VIII

II

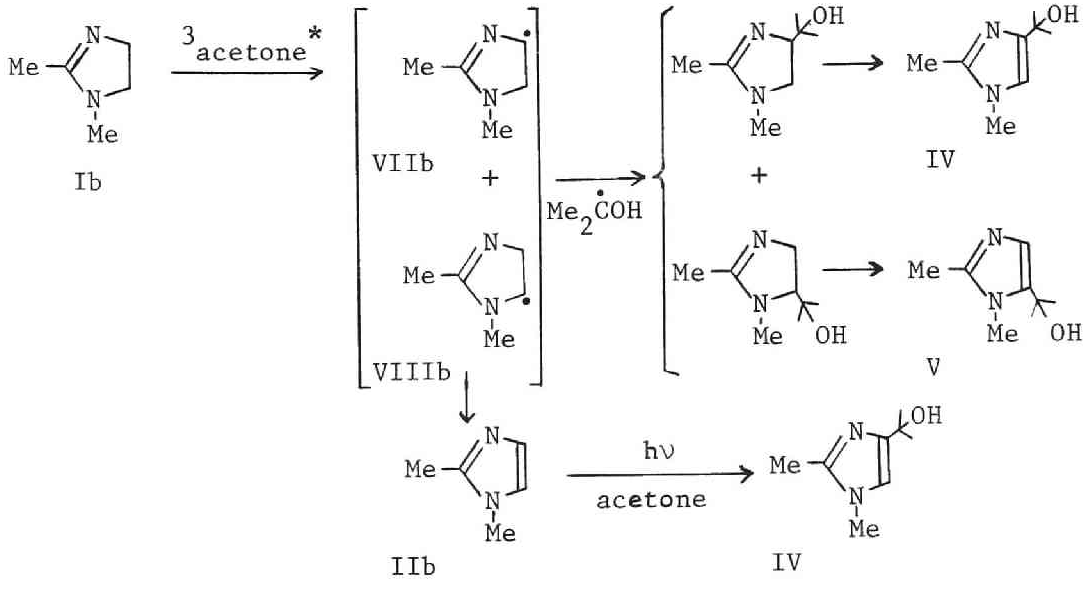
on the AIBN concentration and also on the structural feature of the imidazolines. A difference between the reactivities of Ia and If may be due to the magnitude of the resonance stabilization of the intermediate radicals, VII and/or VIII : i.e., the radicals VIIf and VIIIf are obviously more stabilized by a phenyl group at positions 4 and 5, respectively. More detailed discussion will be described below. The slower dehydrogenation rate in Ig compared with If is probably due to a steric repulsion between a phenyl group at position 5 (or 4) and 1-cyano-1-methylethyl radical produced from AIBN in the abstraction of a hydrogen atom at position 4 (or 5).

3. Discussion

The mechanism of Scheme 1 involving the imidazolinyl radical (VII orVIII), which is formed from the starting imidazoline by hydrogen abstraction with the n, π^* triplet state of acetone, is supported by

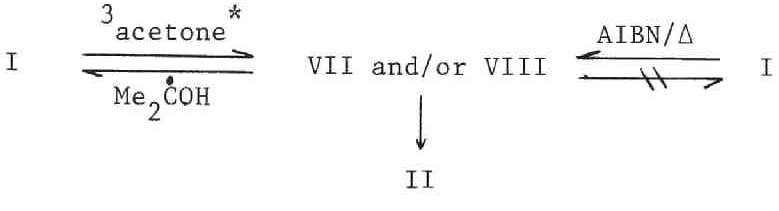
following facts. (1) Imidazoles were also formed by the hydrogen abstraction reaction initiated by AIBN (Table 2). (2) Oxygen, a triplet quencher,[9] inhibited the formation of 2-methylimidazole from 2-methylimidazoline. (3) In some cases coupling products such as III, IV, V and VI were formed as byproducts, which obviously resulted from coupling between the acetone ketyl radical and the imidazolinyl radical VII or VIII followed by dehydrogenation of the coupling products in cases of III, IV and V. Matsuura,et al. have found that irradiation of 1,2-dimethylimidazole(IIb) in acetone gives exclusively IV, and that IV is formed <u>via</u> an unstable oxetane intermediate.[10] Therefore the formation of an almost equal amount of IV and V from Ib should result from coupling between the acetone ketyl radical and the imidazolinyl radicals VIIb and VIIIb, although it may be possible that a part of IV formed results from the photochemical addition of acetone to IIb (Scheme 2).

Scheme 2.



As seen in Table 1 and Table 2, 2-methylimidazoline(Ia) is more susceptible to the photochemical dehydrogenation than amarine(If), but less susceptible to the AIBN-initiated one. Furthermore the cis, trans-isomerization of amarine(If) and isoamarine(Ig), which is accompanied with the dehydrogenation to lophine(IIf), occurs only during irradiation in acetone but not during the AIBN-initiated free radical reaction. These facts can be interpreted by assuming that, in case of photoreaction, the free radical intermediates VII and/or VIII revert in part to the parent imidazoline by a hydrogen transfer from the acetone ketyl radical[11,12] which is known to act as a hydrogen donor as seen in the photoreduction of benzophenone with isopropyl alcohol,[15] and that, in the absence of such a hydrogen donor (AIBN-initiated reaction), the intermediate radicals VII and/or VIII are transformed to an imidazole II without reverting to the parent imidazoline I. These are shown in Scheme 3. As regards the overall reaction from I to II, the imidazole-forming step (VII or VIII $\longrightarrow$ II) may be more important in the photoreaction involving a reverse process from VII or VIII to I than in the AIBN-reaction without such a process. On the contrary, the radical-forming step may be more important in the AIBN-reaction than in the photoreaction.[16]

Scheme 3



In order to ascertain this, the total π electron energies (E_π) of I, VII and II were calculated by HMO method.[17,19] It was assumed from the calculated E_π values for VII and VIII that VII contributes more than VIII to the free radical intermediate. Comparisons of the values $\Delta E_{\pi 1} = E_\pi(VII) - E_\pi(I)$ and $\Delta E_{\pi 2} = E_\pi(II) - E_\pi(VII)$ with the yields of the imidazoles from the imidazolines I are shown in Table 3. The yield of the photochemical conversion to imidazoles decreases in the order of Ia>If>Ib>Ic. This is qualitatively correlated with $E_{\pi 2}$ but not with $E_{\pi 1}$. The decrease in the yield of the photochemical conversion to imidazoles seems to be general for 1-alkylimidazolines as seen in the case of Ib, Id and Ie (Table 1). On the contrary, the yield of the AIBN-initiated conversion to imidazoles seems to be correlated with $\Delta E_{\pi 1}$ rather than $\Delta E_{\pi 2}$. The results led us to conclude that in the photochemical dehydrogenation the resonance stabilization of the product imidazoles, which is represented by a higher $\Delta E_{\pi 2}$ value, is more important, and that in the AIBN-initiated dehydrogenation the resonance stabilization of the intermediate free radical VII, which is represented by a higher $\Delta E_{\pi 1}$ value, is more important. Accordingly, these calculated data do not inconsistent with the mechanism shown in Scheme 3.

In an attempt to confirm further the back reaction of the imidazolinyl radicals, VII or VIII, to I by a hydrogen transfer from the acetone ketyl radical (Scheme 3), an acetone solution of 2-phenylimidazoline(Ic) was irradiated in the presence of MeOD and D_2O with different periods. As seen from Table 4, the incorporation of deuterium

into the recovered Ic obviously indicates that the back hydrogen transfer to VII or VIII by the acetone ketyl radical did occur in the photochemical reaction. It is noted that the deuterium incorporation into Ic was not so much as expected. This is probably due to a slower exchange reaction between the acetone ketyl radical and MeOD or D_2O than the back-transfer reaction.

4. Experimental

All the melting points are uncorrected. The NMR spectra were taken on a NEVA T-60 spectrometer using tetramethylsilane as the internal standard. The IR spectra were measured on a JASCO IRS spectrometer. The UV spectra were obtained with a JASCO ORD/UV-5 spectrometer. Vapor phase chromatography(vpc) was carried out with a Shimadzu GC-2C apparatus (on Apiezon Grease L) using helium as carrier gas. Thin layer chromatography(tlc) was carried out with Merck "Kieselgel GF_{254}", "Aluminiumoxide GF_{254}" or Nagel "Cellulosepulver MN 300 G", using UV light and iodine vapor for compound detection. Column chromatigraphy was carried out with Mallinckrodt silicic acid (100 mesh).

Starting material.

2-Methylimidazoline(Ia) and 2-phenylimidazoline(Ic) were commercially available and used after recrystallization from acetone. Ethylenethiourea(Ih) and ethyleneurea(Ii) were also commercially available and used without further purification.

1,2-Dimethylimidazoline(Ib) was prepared by applying the method reported by King and McMillan.[21] Thus, to 5 g of N-methylethylenediamine was added 7 g of acetic anhydride at room temperature and the mixture was heated at 170-190°C for 1 hr. After cooling 3 g of magnesium powder was added. The mixture was heated at about 300°C for 1 hr, then 1,2-dimethylimidazoline formed was distilled out. It was further

refined by vacuum distillation to give pure Ib as a colorless liquid (3 g; 46 %) which gave satisfactory spectral and analytical data; bp ca. 70°C/14 mm (lit.[22] 60-62°C/12 mm); n_D^{26} 1.4759 (lit.[22] n_D^{20} 1.4766); picrate, mp 137-138.5°C (lit.[22] 145-147°C).

1-Methyl-2-phenylimidazoline(Id) was prepared by applying the method of Hill and Aspinall.[23] Thus, 18.4 g of benzoic acid was added to 11.2 g of N-methylethylenediamine and the mixture was heated at 150-170°C for 1.5 hr, then at 200-220°C for 2 hr. The product was refined by repeating vacuum distillation to give Id as colorless liquid (5 g; 21 %); bp ca. 95°C/4 mm; IR(neat) 2850, 1605, 1270, 1065, 775 and 700 cm^{-1}; NMR ($CDCl_3$) τ 2.30-2.69 (m, 5H), 5.88-6.80 (m, 4H) and 7.20 (s, 3H); m/e 160 (M^+). Found : C, 75.25; H, 7.79; N, 17.31 %. Calcd. for $C_{10}H_{12}N_2$: C, 74.96; H, 7.55; N, 17.49 %. It gave a picrate, mp 121-123°C.

1-(β-hydroxyethyl)-2-phenylimidazoline(Ie) was prepared analogously from N-(β-hydroxyethyl)ethylenediamine and benzoic acid, as colorless crystals; mp 103-104.5°C; IR (nujol) 3200, 1590, 1570, 1235, 765 and 685 cm^{-1} ; NMR($CDCl_3$) τ 2.33-2.72 (m, 5H), 5.90-7.00 (m, 8H) and 6.17 (s, 1H). Found : C, 69.68; H, 7.13; N, 14.81 %. Calcd. for $C_{11}H_{14}ON_2$: C, 69.50; H, 7.37; N, 14.71 %.

Amarine(If) was prepared according to the method of Strain[24] and purified by repeating recrystallization from anhydrous ether. Isoamarine(Ig) was prepared by isomerizing amarine with sodium methoxide at 160-170°C,[25] and purified by repeating recrystallization from ethanol.

General procedure for photodehydrogenation.

The following procedure was used for experiments listed in Table 1. A solution of about 2 g of an imidazoline in 220 ml of acetone was irradiated with a 10 W low-pressure mercury lamp (Vycor housing) under nitrogen at room temperature for 24 hr or more. After irradiation the solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column. The yield of products was obtained by NMR or vpc analysis of the reaction mixture or by product isolation.

Isolation and identification of dehydrogenation products.

2-Methylimidazoline(Ia). The residue obtained from 2.10 g of Ia was chromatographed on 70 g of silica gel. Elution with 100 ml of acetone yielded 350 mg of an oil which was again chromatographed to give 150 mg of pinacol (identified by IR and NMR). Further elution with 200 ml of acetone-ethanol (1 : 1) yielded 1.18 g of a solid. Recrystallization from chloroform gave 400 mg of 4-(α-hydroxyisopropyl)-2-methylimidazole(III) as colorless crystals which were identical with an authentic sample [10] (IR, NMR and mixed mp). Crystals obtained from the mother liquor were recrystallized from benzene to give 2-methylimidazole(IIa) as colorless crystals, identical with a commercial authentic sample (IR, NMR and mixed mp). Further elution of the chromatogram yielded 680 mg of a solid which was identified as IIa. The yields of the products were determined by NMR analysis of the product mixture with an internal standard (acenaphthene). The yield of pinacol was 6 % assuming that 1 mol of Ia gives 1 mol of pinacol.

1,2-Dimethylimidazoline(Ib). The residue obtained from 1.85 g of Ib was chromatographed on 50 g of silica gel. Elution with 300 ml of chloroform and acetone (1 : 1) yielded 300 mg of an oil which was shown by IR and NMR to contain pinacol. Further elution with 300 ml of acetone yielded 110 mg of a solid which were recrystallized from acetone to give 10 mg of 1,2-dimethyl-5-(α-hydroxyisopropyl)imidazole (V) as colorless crystals; mp 179-181°C; IR (nujol) 3200, 1150 and 810 cm^{-1} ; NMR ($CDCl_3$) τ 3.33 (s, 1H), 6.25 (s, 3H), 6.79 (s, 1H), 7.67 (s, 3H) and 8.39 (s, 6H) ; m/e 154 (M^+). The NMR and mass spectra are very similar to those of IV.[10]

Found : C, 62.67; H, 9.23; N, 17.71 %. Calcd. for $C_8H_{14}ON_2$: C, 62.30; H, 9.15; N, 18.15 %.

The mother liquor was shown by IR and NMR analyses to consist of 1,2-dimethylimidazole(IIb), 1,2-dimethyl-4-(α-hydroxyisopropyl)imidazole(IV) and V. Compound IIb was isolated by vpc and identified by comparison with an authentic sample[10] (IR). Compound IV was dehydrated during vpc to give 1,2-dimethyl-4-isopropenylimidazole, as already

known,[10] which was identified by comparison with an authentic sample[10] (IR). Further elution of the chromatogram with acetone yielded a mixture of IIb, IV and V, identified by tlc. The yields of these products were determined by vpc analysis with an internal standard (p-t-butylphenol). NMR analysis of the product mixture showed the formation of pinacol (0.3 mol/mol of IIb).

2-Phenylimidazoline(Ic). The residue obtained from 2.60 g of Ic was chromatographed on 60 g of silica gel. Elution with chloroform and ethanol (9 : 1) yielded 2-phenylimidazole(IIc), identical with a commercial authentic sample (IR, NMR and mixed mp). The yield of IIc was determined by vpc analysis with an internal standard (diphenyl).

1-Methyl-2-phenylimidazoline(Id). The residue obtained from 2.03 g of Id was chromatographed on 60 g of silica gel. Elution with chloroform yielded 1-methyl-2-phenylimidazole(IId) as a liquid; bp 140-145°C (bath temperature)/3 mm (lit.[26] bp 175°C/15 mm); IR(neat) 1500, 1480, 1410, 1270, 770, 715 and 700 cm^{-1} ; NMR($CDCl_3$) τ 2.21-2.60 (m, 5H), 2.83 (d, 1H, J=1 Hz), 3.01 (d, 1H, J=1 Hz) and 6.25 (s, 3H). It gave satisfactory elemental analyses. The yield of IId shown in Table 1 was based on the product isolated and the recovered Id was analyzed by vpc.

Amarine(If) and isoamarine(Ig). The residues obtained from 2.09 g of If and 2.02 g of Ig were chromatographed on 70 g of silica gel, respectively. Elution with chloroform gave lophine(IIf), Ig and If, successively, which were identical with authentic samples (IR and NMR). The yield of IIf was determined by UV analysis in ethanol and the recovered materials by NMR analysis with an internal standard, 2-methylimidazoline (in carbon tetrachloride-dimethylsulfoxide-d_6).

2-Hydroxyimidazoline(Ii). A suspension of Ii (1.63 g) was irradiated. The insoluble solid separated by filtration was found to be mainly the recovered Ii (IR and NMR). The residue from the filtrate was chromatographed on 60 g of silica gel. Elution with acetone yielded VI as colorless crystals; mp 198-201°C ; IR(nujol) 3300, 1655 and 1175 cm^{-1} ; NMR(DMSO-d_6) τ 5.26 (s, 4H), 6.63 (s, 2H) and 8.86 (s, 12H).

Found : C, 53.48; H, 8.94; N, 13.75 %. Calcd. for $C_9H_{18}N_2O_3$: C, 53.44; H, 8.97; N, 13.85 %.

This compound showed a UV maximum at 275 nm in ethanol identical with that of Ii. Further elution yielded additional Ii. The yields listed in Table 1 were based on product isolation.

Photoreaction of 2-methylimidazoline(Ia) under oxygen.

A solution of 2.08 g of Ia in acetone was irradiated for 24 hr under similar conditions except oxygen-bubbling instead of nitrogen. After removal of the solvent under reduced pressure, the residue was chromatographed on 60 g of cellulose powder (Whatman CF 11). Elution with 1200 ml of benzene-chloroform (1 : 4) yielded 530 mg (27 %) of Ia, identified by IR. Further elution with 1000 ml of acetone-ethanol (1 : 1) yielded 1.12 g of an oil. Vacuum distillation of the oil gave 400 mg (12 %) of 2-methylimidazolinium acetate, mp 95-96°C (lit.[27] mp 94.5-95.5°C), which was identical with an authentic sample (IR and NMR).

Hydrogen abstraction of imidazolines initiated with AIBN.

A given amount of each imidazoline was dissolved in 150 ml of acetonitrile. The solution was heated at 68 ± 1.5 C under nitrogen and a given amount of azobisisobutyronitrile was added. After standing at the same temperature for 24 hr, the mixture was worked up in the same manner as on the photoreaction. The results are shown in Table 2. 2-Methylimidazole was analyzed by NMR with an internal standard, pinacol, and lophine by UV in ethanol.

Deuterium incorporation experiment.

A solution of ca. 100 mg of 2-phenylimidazoline(Ic) in a mixture of acetone and MeOD and D_2O placed in a Pyrex tube was sealed after bubbling nitrogen and irradiated externally. After evaporation of the mixture under reduced pressure, the residue was dissolved in chloroform and washed three times with 2 ml of water to remove any deuterium bound to nitrogen atom of Ic. The solution was evaporated after drying with anhydrous sodium sulfate. The recovered Ic in the residue was isolated by preparative tlc (Al_2O_3 ; acetone-ethanol (3 : 1)) and recrystallized from benzene-petroleum ether. The pure Ic thus obtained was analyzed

on Hitachi RMS-4 mass spectrometer. The molecular ion region was scanned several times for each sample. Deuterium contents were calculated by comparing peak heights with those of a non-deuterated sample of Ic.

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3. Various hydroaromatic compounds can photoaromatize from their excited states[4] or with the aid of hydrogrn abstracting agents such as excited carbonyl compounds and thiyl radicals.[5]
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11. In the cases of amarine(If) and isoamarine(Ig), it was shown that intermediate radicals, VIIf and/or VIIIf, revert only to amarine but not to isoamarine.[8] The formation of isoamarine(Ig) during irradiation of amarine was found to arise from the excited of amarine iyself.[7,8]

12. The bond dissociation energy of the acetone ketyl radical ($Me_2\dot{C}O$-H) appears lower than that of $Me_2C(CN)$-H, since that of $\cdot CH_2O$-H (29 kcal/mol[13]) is much lower than that of H-CH_2CN (ca. 86 kcal/mol[14]).

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16. This is similar to the notion of a successive reaction:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \qquad B \xrightarrow{k_2} C$$

If the process B $\longrightarrow$A is much faster than the process B $\longrightarrow$C, the latter process should be rate-determining (case 1). On the contrary, if the process B $\longrightarrow$A is much slower than the process B $\longrightarrow$C, the former process should be rate-determining (case 2). The photo-

chemical reaction is similar to case 1 and the AIBN-initiated one to case 2.

17. Parameters were selected from ones presented by Streitwieser[18a] except for parameters concerning sulfur bonds.[18b] The use of the E_π value for VIII for the following discussion does not alter the conclusion.

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20. When the twisted angle is assumed to be 25°, $\Delta E_{\pi 2}$ value is calculated as 2.58445β. G. Rasch [Z. Physik. Chem., 219, 180 (1962)] assumed the twisted angle of phenyl groups of cis-stilbene as 26±4 .

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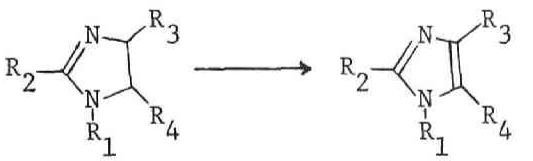
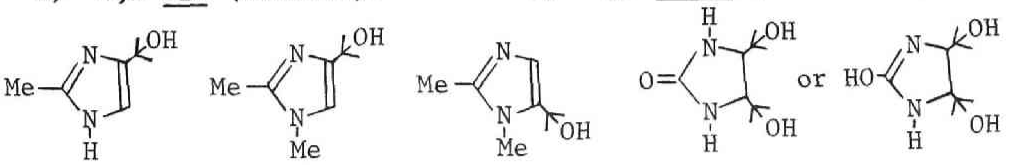
Table 1. Photochemical dehydrogenation of imidazolines I to imidazoles II in acetone.



I II

	I				Irradn. time (hr)	Recovered I (%)	Yield of II (%)[c]	Other product (%)[c]
	R_1	R_2	R_3	R_4				
Ia	H	Me	H	H	24	0	60	III (9)
Ib	Me	Me	H	H	24	0	22	IV (6) + V (5)
Ic	H	Ph	H	H	24	58	15	
					75	36	36	
Id	Me	Ph	H	H	24	26	18	
Ie	$(CH_2)_2OH$	Ph	H	H	50	37	20	
If	H	Ph	Ph	Ph[a]	24	25	35	Ig (16)
Ig	H	Ph	Ph	Ph[b]	24	16	28	If (27)
Ih	H	SH	H	H	24	100	0	
Ii	H	OH	H	H	24	36	0	VI (20)

a) 4,5-cis (amarine). b) 4,5-trans (isoamarine)



III IV V VI

c) Based on the starting imidazolines.

Table 2. AIBN-initiated dehydrogenation of imidazolines to imidazoles.[a]

Imidazoline	Concentration ($\times 10^{-2}$ M) Imidazoline	AIBN	Molar ratio of AIBN/Imidazoline	Yield of Imidazole (%)[b]
2-Methyl- (Ia)	10.25	9.38	0.92	4.0
	9.60	4.69	0.49	0
cis-2,4,5-Triphenyl- (If)	2.72	3.70	1.36	26.0
	2.67	1.85	0.69	12.0
	2.71	0.37	0.14	4.5
trans-2,4,5-Triphenyl- (Ig)	2.68	8.66	3.24	3.2
	2.73	4.89	1.79	2.0

a) Reaction conditions: 68±1.5°C in acetonitrile under nitrogen.

b) Based on the starting imidazolines.

Table 4. Deuterium incorporation into 2-phenylimidazoline (Ic) during photolysis in the presence of MeOD and D_2O in acetone.

Concn. of Ic ($\times 10^{-2}$ M)	Solvent (ml) Acetone	MeOD	D_2O	Irrad. time (hr)	Ic-d_1[a] (%)
4.75	5	10	0	41[b]	0.2 ± 0.1
3.63	5	10	5	163[c]	1.9 ± 0.1
3.43	5	10	5	245[c]	1.6 ± 0.2

continued on the next page

Table 3. Comparison of the yield of imidazoles(II) from imidazolines(I) with $\Delta E_{\pi 1}$ and $\Delta E_{\pi 2}$ values.

Imidazoline	Yield of imidazole(%) Photochemical High concn.[a]	Low concn.[b]	AIBN-initiated[c]	$\Delta E_{\pi 2}(\beta)$[d]	$\Delta E_{\pi 1}(\beta)$[d]
2-Methyl-(Ia)	60	20.0±0.5	4	2.58100	0.67520
cis-2,4,5-Triphenyl-(If)	35	16.1±1.2	26	2.53995[e]	1.21005
1,2-Dimethyl-(Ib)	22	—	—	2.55070	0.69020
2-Phenyl-(Ic)	15	—	—	2.52744	0.73246

a) Taken from the data of Table 1 (irradiation time, 24 hr).

b) A ca. 10^{-3} M acetone solution was externally irradiated using a merry-go-round apparatus and the yields of imidazoles formed were determined by UV analysis.

c) Taken from the data of Table 2.

d) See text.

e) Calculation was done by assuming that two phenyl groups at positions 4 and 5 are twisted 30° from the plane of the imidazole ring.[20]

Table 4.(continued)

a) Deuterium analysis was done by mass-spectrometry.

b) Externally irradiated with a 100 W high-pressure mercury lamp (Pyrex filter).

c) Externally irradiated with a 450 W high-pressure mercury lamp (Pyrex filter).

C H A P T E R V

On the Applicability of Excited Acetone to Induce Photoaromatization of Dihydroheteroaromatics

Photoaromatization of various dihydroheteroaromatics and some carbocyclic dihydroaromatics with excited acetone was examined. Among the tested compounds, indoline, 2,3-dihydro-2-methylbenzofuran, and 9,10-dihydroanthracene were found to be photoaromatized. 2-Thiazolines, 2-oxazolines, 2-isoxazolines, 9,10-dihydrophenanthrene, 2,3-dihydro-5,6-dimethylpyrazine, 3,4-dihydro-1-methylisoquinoline, and 6-methyl-3(2H)-pyridazinone did not undergo photoaromatization, but recovered unchanged or underwent their own photochemical reactions.

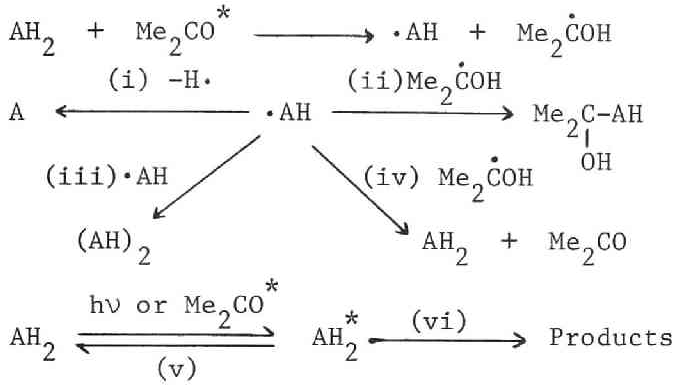
1. Introduction

In the preceding chapter, the author has reported that excited states of acetone could be used to dehydrogenate imidazolines to imidazoles. The author's attention, then, was focused to see whether this photoaromatization could be extended to other dihydroaromatics. The present chapter shows that it is not always the case but various types of reactions take place, although the photoaromatization occurs in some cases. Interpretation of the results with the Hückel molecular orbital (HMO) energy was attempted with some success.

2. Results and discussion

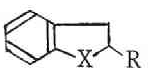
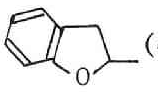
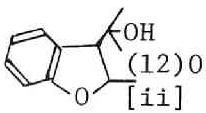
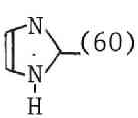
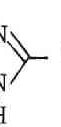
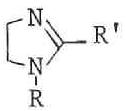
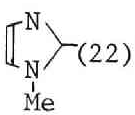
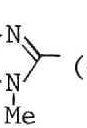
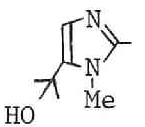
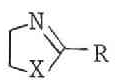
An acetone solution of various dihydroheteroaromatics (AH_2), including a few carbocyclic dihydroaromatics, was irradiated with light mainly at 2537 Å and the products were separated by chromatographic methods. The results are summarized in Table 1, which also includes the results obtained with 2-imidazolines (No. 3-5)[1] for comparison. Various types of reactions occurred and they can be classified into the following six categories. A hydroaromatic radical(·AH), which is produced by hydrogen abstraction with excited acetone from AH_2, may undergo four types of processes ; (i) dehydrogenation to an aromatic compound (A), (ii) coupling with the acetone ketyl radical, (iii) dimerization, and (iv) regeneration of AH_2 by hydrogen tranfer from the acetone ketyl

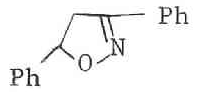
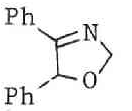
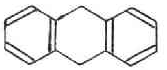
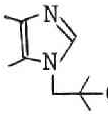
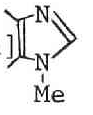
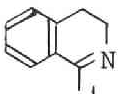
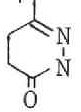
radical. Process (iv) has been proved to occur in part in the case of imidazolines.[1] Other processes will involve the excited states (AH_2^*) of the substrate itself; namely, (v) deactivation to AH_2 and (vi) its own photochemical reaction leading to products.



Only indoline(No. 1), 2,3-dihydro-2-methylbenzofuran(No. 2), and 9,10-dihydroanthracene(No. 12) gave the corresponding aromatized product or its further photolysis product, e.g. dianthracene from dihydroanthracene.[10] The intermediary formation of radical ·AH is demonstrated in the latter two cases giving a cross-coupling product and a dimer, respectively. While 2-methyl-2-thiazoline(No. 6) and 3,5-diphenyl-2-isoxazoline (No. 10) gave N-vinylthioacetamide[4] and 4,5-diphenyl-3-oxazoline,[6] respectively, other compounds (No. 7, 9, 12, 14 and 15) were unreactive under the conditions except 2-methyl-2-oxazoline(No.8) which gave a complex mixture of products. The photochemical isomerization of 2,3-dihydro-5,6-dimethylpyrazine(No. 13) to 1,4,5-trimethylimidazole has already been reported.[11] Since the transformation of this imidazole to the imidazole-acetone adduct, 1-(2-hydroxy-2-methylpropyl)-4,5-dimethylimidazole, did not occur under the similar photo-

Table 1. Photochemical Reactions of Dihydroaromatics (AH_2) in Acetone at 2537 Å.

No.	AH_2	Concn. g/220 ml	Irrad. time(hr)	Recovered (%)(iv or v)	Products(% yield)[a] [Type of product][b]	HMO calculation[c] $\Delta E_{\pi 1}(\beta)$	$\Delta E_{\pi 2}(\beta)$
1	 R=H, X=NH[2]	0.70	21	0	indole(46)[i]	0.61668[d]	2.71792
2	R=Me, X=O[3]	2.19	186	31	 (4)[i]  (12)[ii]	0.72735[d]	2.41491
3	R=H, R'=Me[1]	2.09	26	0	 (60)[i]  (9)[ii]	0.67520	2.58100
4	 R=Me, R'=Me[1]	1.85	24	0	 (22)[i]  (6)[ii]  (5)[ii]	0.69020	2.55070
5	R=H, R'=Ph[1]	2.60	75	36	2-phenylimidazole(36)[i]	0.73246	2.52744
6	 R=Me, X=S[4]	2.26	113	e	N-vinylthioacetamide (14)[4][vi]	0.75309[d]	2.39559
7	R=Ph, X=S[4]	2.39	48	f	———	——	——
8	R=Me, X=O[5]	2.80	119	g	———	——	——
9	R=Ph, X=O[5]	2.20	45	f	———	0.68715[d]	2.28541

10		6	2.26	52	29	 (7)[6][vi] etc.	——	——
11		2	3.10	88	19	dianthracene(15)[i] 9,10,9',10'-tetrahydro-dianthranyl(15)[iii]	1.09174	2.22194
12		2	2.04	24	f	——	0.63098	2.50456
13		7	2.17	22	e	 (19)[ii]  (40)[vi]	0.73885	2.94457
14		8	2.24	142	f	——	0.68485[d]	2.67979
15		9	1.86	48	f	——	0.74023[d]	2.60967

a) Based on the initial amount of the starting material. b) A[i], HA-C(OH)Me_2[ii], $(HA)_2$[iii], and others[vi]. c) See Part I Chapter IV for the method of calculation. E_π: total π-electron energy of the aromatic system ($E_{\pi A}$), ·AH($E_{\pi\cdot AH}$), or AH_2($E_{\pi AH_2}$). $\Delta E_{\pi 1}=E_{\pi\cdot AH}-E_{\pi AH_2}$. $\Delta E_{\pi 2}=E_{\pi A}-E_{\pi\cdot AH}$.

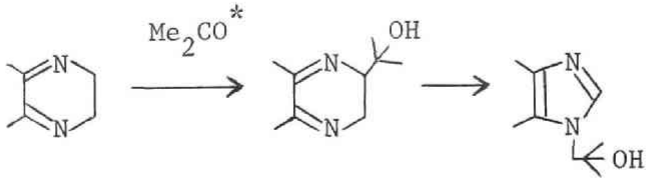
d) Intermediates having the radical center at 3 position for indoline, 2 for 2,3-dihydro-2-methylbenzofuran, 4 for 2-methyl-2-thiazoline, 4 for 2-phenyl-2-oxazoline, 3 for 3,4-dihydro-1-methylisoquinoline, and 5 for 4,5-dihydro-6-methyl-3(2H)-pyridazinone were assumed as ·AH on the basis of their larger π-delocalization energy than those having the radical center at another position.

e) The starting material decomposed during column chromatography on silica gel.

f) Essentially no reaction occurred judging from NMR, IR and tlc analyses of the photolysate.

g) It gave a complex mixture which contained no 2-methyl-2-oxazole.

lytic conditions, it is assumed that the adduct is formed by a similar photoisomerization of the dihydropyrazine-acetone adduct [type (ii) product] as depicted below.



Although the present data are insufficient to make a proper prediction about the reaction courses which dihydroaromatic compounds will follow, the author has attempted to interpret the results, particularly on photoaromatization, in terms of HMO π-electron energy (Table 1). The author showed in the preceding chapter that $\Delta E_{\pi 2}$ value, which implies the stabilization energy of π-electron for the aromatization step (·AH → A), has a more important meaning to the photodehydrogenation of imidazolines to imidazoles than $\Delta E_{\pi 1}$ value which might contribute to lowering the activation energy of the hydrogen abstraction step (AH_2 → ·AH). This argument may be valid in the case of the five-membered dihydroheteroaromatics. Thus, indoline(No. 1) having a higher $\Delta E_{\pi 2}$ value than those of imidazolines is easily photoaromatized and 2,3-dihydro-2-methylbenzofuran(No. 2) having a somewhat lower $\Delta E_{\pi 2}$ value undergoes slow photoaromatization. 2-Methyl-2-thiazoline(No. 6) and 2-phenyl-2-oxazoline(No. 9) having a low $\Delta E_{\pi 2}$ value suffered no photoaromatization. These results are not interpreted in terms of the $\Delta E_{\pi 1}$ value. Attempts to interpret the data for the six-membered hydroaromatics in terms of either $\Delta E_{\pi 1}$ or $\Delta E_{\pi 2}$ value proved unsuccessful.

3. Experimental

All the melting points are uncorrected. NMR spectra were taken on a NEVA T-60 spectrometer with tetramethylsilane as the internal standard. IR spectra were measured on a JASCO IRS spectrophotometer. Mass spectra were determined on a HITACHI RMS-4 spectrometer. Vapor phase chromatography (vpc) was carried out with a Shimadzu GC-2C. Unless otherwise specified, column chromatography (cc) was carried out with Mallinckrodt silica gel (100 mesh) and thin layer chromatography (tlc) with Merck Kieselgel GF_{254}.

Materials.

The starting materials were commercially available or prepared according to the methods of literatures cited in Table 1.

Irradiation.

A given amount (Table 1) of the substrate was dissolved in 220 ml of acetone and the solution was irradiated internally with a 10-W low-pressure mercury lamp (Vycor housing) under bubbling nitrogen with external cooling with tap water. After evaporation of the solvent under reduced pressure, the residue was submitted to separation in the following way.

Isolation and characterization of photoproducts.

Indole was isolated by vpc (Silicone DC 550, 40-60 mesh; helium, 1.1 kg/cm^2 gauge; 140°C), mp 48.5-51°C (lit.[12] mp 52°C), which was identical with an authentic sample (IR). The yield of indole was determined by vpc using diphenyl as the internal standard.

The crude photolysate obtained from 2,3-dihydro-2-methylbenzofuran was chromatographed on 70 g of silica gel. Elution with 300 ml of petroleum ether gave 90 mg of 2-methylbenzofuran. The IR spectrum was identical with the Sadtler Standard Spectrum of this compound. Further elution with 1300 ml of petroleum ether afforded 680 mg of the starting material (tlc and IR). After elution of 440 mg of unidentified products, 380 mg of 2,3-dihydro-3-(α-hydroxyisopropyl)-2-methylbenzofuran was eluted with 1100 ml of benzene-chloroform (1 : 1),

which was further purified by preparative tlc (benzene-chloroform 5 : 1) and distilled to give a colorless oil ; bp 75-80°C (bath temp.)/2 mmHg ; ν_{max}(neat) 3470, 1595, 1240, 1135, 750 cm^{-1} ; λ_{max}(EtOH) 289 (ε 3600), 283 (ε 4300) nm : τ ($CDCl_3$) 2.60-3.34 (4H, m, aromatic H), 5.18 (1H, d-q, J=3Hz, J'=7 Hz, -C<u>H</u>-O), 7.02 (1H, slightly diffused d, J=3 Hz, -C<u>H</u>-CH-O), 7.83 (1H, broad s, disappeared on deuteration, O<u>H</u>), 8.63 (3H, d, J=7 Hz, $C\underline{H}_3$-CH-), 8.78 (6H, d, J=1.5 Hz, $(C\underline{H}_3)_2$-C-) ; m/e (rel. int.) 192 (M^+, 11), 134 ($M^+-(CH_3)_2CO$, 100), 133 ($M^+-(CH_3)_2COH$, 83), 119 (134-CH_3, 79), 105 (73), 91 (58), 59 (70).

Found : C, 74.77; H, 8.42 %. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39 %. Further elution with more polar solvents (chloroform and acetone) gave 1.20 g of a mixture of unidentified products.

During the photolysis of 9,10-dihydroanthracene, dianthracene (450 mg) precipitated as colorless crystals which were identical with an authentic sample[10] (IR). After removal of dianthracene and the solvent, the residue was chromatographed on 90 g of silica gel. Elution with 1100 ml of petroleum ether yielded 590 mg of the recovered starting material (tlc and IR). Further elution with 2400 ml of the same solvent gave 470 mg of 9,10,9',10'-tetrahydrodianthranyl, mp 273-274°C (lit.[13] mp 256-257°C), which was identical with an authentic sample[13] (IR, NMR). Further elution with more polar solvents (benzene and chloroform) gave 1.57 g of a mixture of unidentified products.

The photolysate from 2,3-dihydro-5,6-dimethylpyrazine was found by NMR analysis to consist of mainly three components, the starting material,1,4,5-trimethylimidazole, and 1-(2-hydroxy-2-methylpropyl)-4,5-dimethylimidazole, in the ratio of 0.8 : 2.6 : 1.6 . The product mixture was chromatographed on 80 g of neutral alumina (Merck). Elution with 1000 ml of benzene-chloroform (2 : 1) gave 90 mg of a mixture of unidentified products. Further elution with 2200 ml of the same solvent afforded 870 mg of crude 1,4,5-trimethylimidazole, which was purified by preparative tlc (Aluminiumoxide GF_{254} Type E, Merck; chloroform-acetone, 2 : 1). Picrate, mp 216-217.5°C (lit.[11] mp 219-220°C) The NMR and IR spectra were consistent with those reported.[11]

Further elution with 1800 ml of benzene-chloroform (1 : 2) and 1000 ml of chloroform yielded 610 mg of 1-(2-hydroxy-2-methylpropyl)-4,5-dimethylimidazole, which was purified by preparative tlc as above mentioned. A colorless viscous oil crystallized on standing ; mp 90.5-92.5°C ; ν_{max}(neat) 3150, 1500, 1220, 1180, 915, 725 cm^{-1} ; λ_{max}(EtOH) 226 (ε 5600) nm ; m/e (rel. intens.) 168 (M^+, 100), 110 ($M^+-(CH_3)_2CO$, 93), 109 ($M^+-(CH_3)_2CHO$, 89), 95 (110-CH_3, 76), 59 (67) ; τ ($CDCl_3$) 2.64 (1H, s, -C<u>H</u>=), 4.86 (1H, s, disappeared on deuteration, O<u>H</u>), 6.28 (2H, s, -C<u>H</u>$_2$-), 7.90 (6H, s, =C-C<u>H</u>$_3$), 8.80 (6H, s, (C<u>H</u>$_3$)$_2$-C-).

Found : C, 64.00; H, 9.66; N, 16.77 %. Calcd. for $C_9H_{16}N_2O$: C, 64.25; H, 9.59; N, 16.65 %.

Further elution with more polar solvents (ethanol) gave 370 mg of a mixture of unidentified products. The starting dihydropyrazine decomposed during chromatography and could not be recovered.

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PART II

CHAPTER I

The Photochemical Addition of Acrylonitrile to Imidazoles

Acrylonitrile photochemically adds to N-unsubstituted imidazoles resulting in α-cyanoethylation both in ethanol and in acetonitrile. Thus, 2-phenylimidazole(1) gave 2-[4(or 5)-(2-phenylimidazolyl)]-propionitrile(3) and 2-[2-(2-phenyl-2H-imidazolyl)]propionitrile(4) and 2,4,5-triphenylimidazole(2) gave 2-[2-(2,4,5-triphenyl-2H-imidazolyl)]propionitrile(5). On the other hand, acrylonitrile photochemically reacts with 1-methyl-2,4,5-triphenylimidazole(6) resulting in either cycloaddition in ethanol to give two cycloadducts 7a and 7b or formation of 1-methyl-2,4,4-triphenyl-Δ^2-imidazolin-5-one(8) in acetonitrile. N-Methylimidazole(9) underwent virtually no reaction. The results indicate that the NH proton plays an important role in the α-cyanoethylation. From fluorescence quenching studies and quantum yield measurements, it is suggested that the α-cyanoethylation occurs via a singlet exciplex with a polar character.

1. Introduction

The photochemical reactions of donor-acceptor systems havs recently drawn considerable attention. In the course of photochemical studies of heterocyclic compounds, the author noticed the nature of five-membered heteroaromatics as possible donors, since they are essentially electron-rich. Acrylonitrile(AN) is one of typical acceptors and its photochemical addition to aromatic hydrocarbons leading to [2 + 2] cycloaddition and α-cyanoethylation has been well studied.[1] However, when the present study was initiated, little attention had been drawn to the photochemical reaction between AN and typical electron-rich five-membered heteroaromatics.[2,3]

Recently McCullough, et al. have presented mechanisms involving exciplex intermediates for the photoaddition of AN to naphthalene and indene.[1e] According to their mechanisms α-cyanoethylation products arise from protonation of the exciplex which has an ion pair structure, proton being provided by a hydroxylic solvent in the naphthalene case. Protonation in the indene case, however, occurs intramolecularly (within the exciplex) because indene has a relatively acidic proton (1-H) which naphthalene lacks.

It is now shown that AN photochemically adds to N-unsubstituted imidazoles(1 and 2) resulting in α-cyanoethylation(3,4 and 5) both in ethanol and in acetonitrile, whereas to a N-methylimidazole(6) resulting in either cycloaddition(7) in ethanol or formation of a Δ^2-imidazolin-5-one(8) in acetonitrile. It is suggested that the α-cyanoethylation

of 1 and 2 takes place probably via formation of a polar singlet exciplex followed by intramolecular proton transfer.

2. Results and Discussion

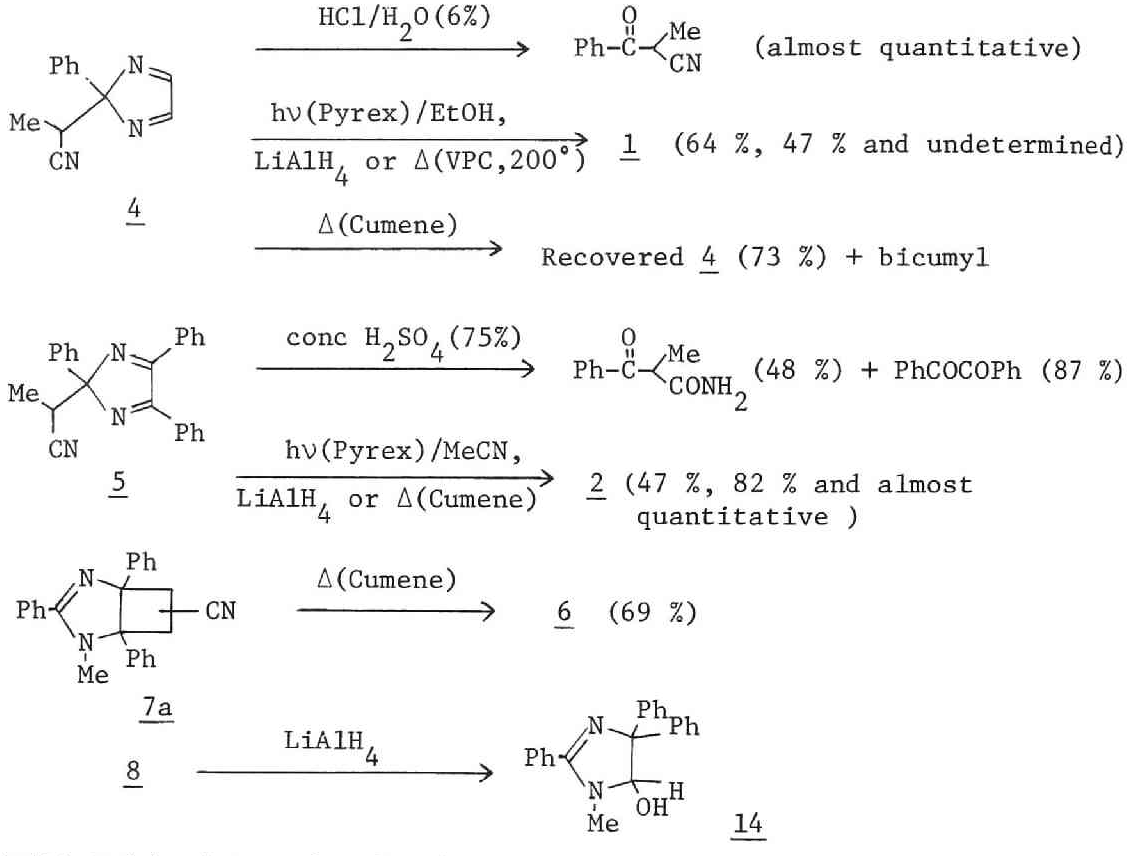
Photoproducts.

A solution of an imidazole in acetonitrile or ethanol was irradiated with a high-pressure mercury lamp (Pyrex filter) in the presence of a large excess of acrylonitrile(AN). After a few minutes the mixture became turbid owing to polymerization of AN. Products were separated mainly by chromatographic procedures after the resultant polymer was separated by filtration. The results are shown in Table 1. Under these conditions. 2-phenylimidazole(1) and 2,4,5-triphenylimidazole(2) gave α-cyanoethylated products (3, 4 and 5) in either a protic or an aprotic solvent,[4] whereas 1-methyl-2,4,5-triphenylimidazole(6) gave cycloadducts 7a and 7b in ethanol and a Δ^2-imidazolin-5-one 8 in acetonitrile. On the contrary, 1-methyl-2-phenylimidazole (9) gave essentially no photoadducts, but only a polymer. These results suggest that the acidic proton of 1 and 2 plays an important role in the formation of α-cyanoethylated products (3, 4 and 5). The same effect of an N-H group was noted in the photoaddition of benzene[5] and naphthalene[6] to pyrroles. In the case of 2, an unknown product 13, which was supposed to be a 1 : 1 adduct similar to 5 judging from NMR analysis was detected as a minor product in addition to the major

product 5.

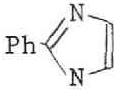
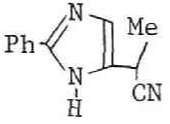
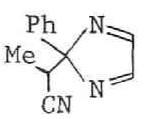
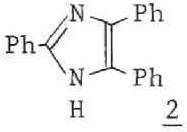
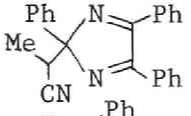
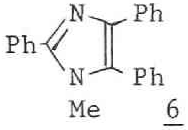
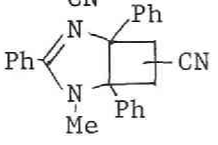
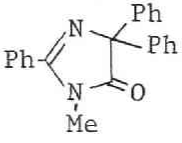
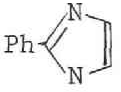
The structures of the photoproducts were assigned on the basis of spectral and chemical evidences. Chemical properties of 4, 5, 7 and 8 are summarized in Scheme 1. The photochemical transformations of 4 and 5 to the corresponding imidazoles (1 and 2, respectively) are probably

Scheme 1.



initiated by intramolecular hydrogen abstraction with a C=N double bond[9] (Scheme 2) by analogy with, for example, the transformation of 1-n-butyl-3,4-dihydroisoquinoline to 1-methyl-3,4-dihydroisoquinoline.[11] The same transformation reaction with $LiAlH_4$ appears to be a nucleophilic substitution with hydride ion (Scheme 2). The IR and UV spectra of 5 were similar to the IR spectrum (between 1625-1475 cm^{-1}) of 2,2,4,5-

Table 1. Photochemical reaction of imidazoles (Im) and acrylonitrile (AN).

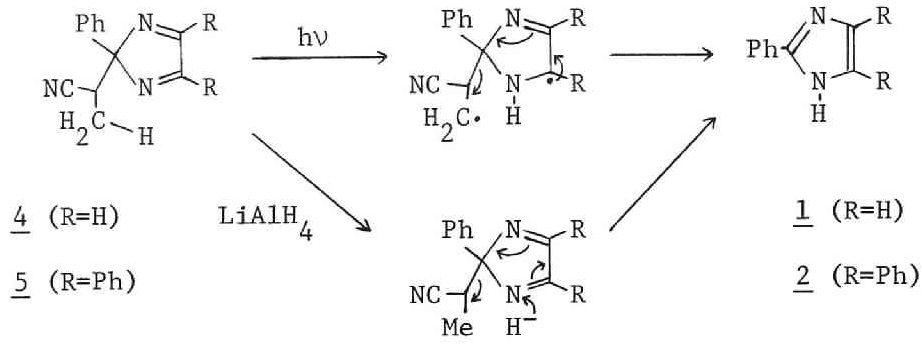
Im ($Mx10^2$)	Mole ratio of AN/Im	solvent	Irrad. time(hr)	Products (%)	Recovered Im(%)
 H 1	29.9	EtOH	18	 3 (2.2)  4 (1.3)	96
	15.5	MeCN	79	3 (2.1) 4 (1.7)	85
 H 2	1.23	EtOH	3.5	 5 (34) 13	27
	0.448	MeCN	4	5 (38) 13	0
 Me 6	2.13	EtOH	4	 7a + 7b[a] (18)[b] c	77[b]
	2.67	MeCN	9	 8 (16) c	55
 Me 9	2.59	EtOH	21	no adducts c	85
	3.48	MeCN	7.5[d]	no adducts	not determined

a) 7a/7b = 3.7 b) Contaminated with a small amount of cis- and trans-1,2-dicyanocyclobutanes.

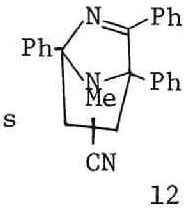
c) Cis- and trans-1,2-dicyanocyclobutanes as side-products.

d) Externally irradiated.

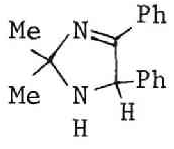
Scheme 2.



tetraphenyl-2H-imidazole[12] and the UV spectrum of 2,2-dimethyl-4,5-diphenyl-2H-imidazole,[10] respectively. These spectral and chemical evidences substantiate the assigned structure. The structure of 4 was unambiguously determined based on the similar chemical properties to those of 5. It should be noted that H-4 and H-5 of 4 appear as two doublets in the NMR spectrum (see experimental section) because of their noneqivalency due to the asymmetric α-cyanoethyl group. That the [2 + 2] adducts (7a and 7b) does not have structures of [2 + 4] adducts(12) were determined by the UV spectra of 7a and 7b which are similar to those of 2-phenylimidazolines but not to those of 15, etc., (See experimental section).



12



15

Mechanistic consideration.

The photochemical additions of AN to aromatic hydrocarbons leading to [2 + 2] cycloaddition and α-cyanoethylation are, in general, interpreted in terms of exciplex formation.[1] Possible pathways for the photochemical addition of AN to imidazoles are shown in Scheme 3.

Mechanisns for the formation of Δ^2-imidazolin-5-one(8) will be described in detail in the next chapter.

An exciplex, which may be formed by complexing of an excited imidazole to AN or by excitation of a ground state complex between an imidazole and AN,[#] should have a charge-transfer character as represented by formula 10 which could also be a solvated or dissociated ion pair. With N-unsubstituted imidazoles 1 and 2, which have an acidic proton (NH), the radical ion pair 10 undergoes proton transfer to give a radical pair 11 which finally gives the α-cyanoethylated products (3, 4 and 5). With 1-methyl-2,4,5-triphenylimidazole(6) the exciplex collapses to the cycloadducts 7a and 7b, while with 9 the exciplex intermediate deactivates exclusively to the ground state of 9 and AN. This mechanism is also consistent with the formation of a large amount of polymer, because AN is known to undergo both radical and anionic polymerization.[7]

According to a report,[1a] the absorption spectra of solutions containing acrylonitrile and benzene, naphthalene, or indene indicate no charge-transfer interaction in the ground states. In the present case, a red-shift of the absorption maximum of 1, 2 and 6 with increasing amount of AN in ethanol was observed, showing the appearance of two isosbestic points (Fig. 1-3 and Table 2). A similar red-shift was also observed in acetonitrile. Consequently, the λ_{max} of 2 and 6 in neat AN was shifted to a longer wavelength than that in EtOH or in MeCN,

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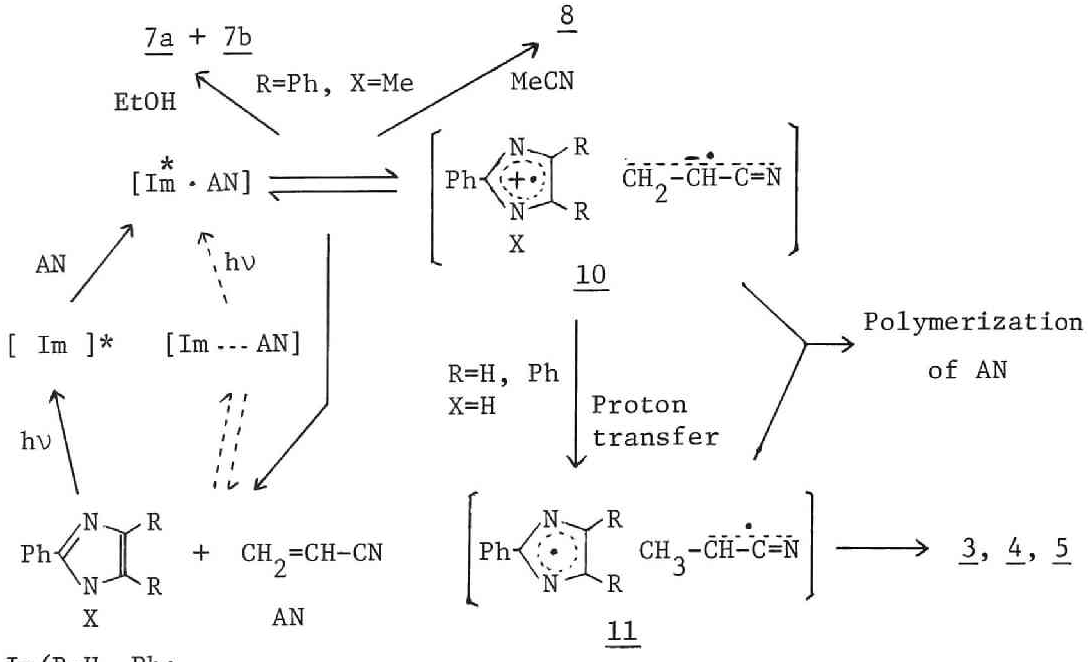
[#] The latter process seems unlikely as described below.

Scheme 3



but this fact is not explicable in terms of the dielectric constants of solvents (Table 3). These observations appear to indicate the presence of an ground-state interaction between AN and the imidazoles. Assuming the following equilibrium, the equilibrium constant (K) and

$$\text{Im} + \text{AN} \underset{}{\overset{K}{\rightleftharpoons}} [\ \text{Im} \cdots \text{AN}\ ]$$

the molar extinction coefficient of a 1 : 1 complex (ε_c) were estimated by the Rose-Drago method.[8] (Table 2). However, since these spectral changes of imidazoles 1, 2 and 6 in various solvents (Fig.1-3 and Table 3) are small, the spectral changes might be simply due to the interaction with the solvent, but not to the formation of a simple 1 : 1 complex in their ground state.

It was found that the fluorescence emission of 2 was quenched

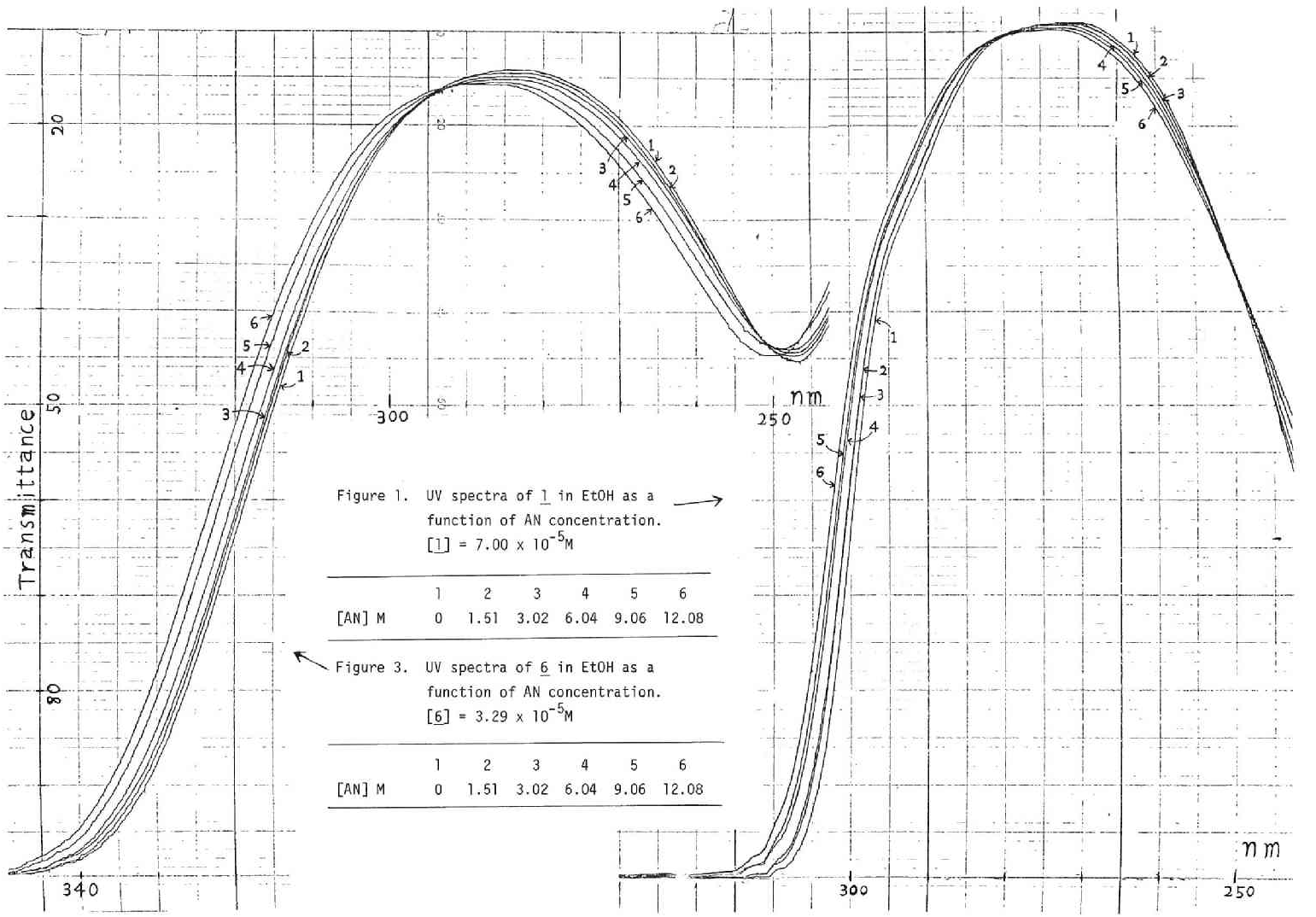


Figure 1. UV spectra of 1 in EtOH as a function of AN concentration.
[1] = 7.00×10^{-5}M

	1	2	3	4	5	6
[AN] M	0	1.51	3.02	6.04	9.06	12.08

Figure 3. UV spectra of 6 in EtOH as a function of AN concentration.
[6] = 3.29×10^{-5}M

	1	2	3	4	5	6
[AN] M	0	1.51	3.02	6.04	9.06	12.08

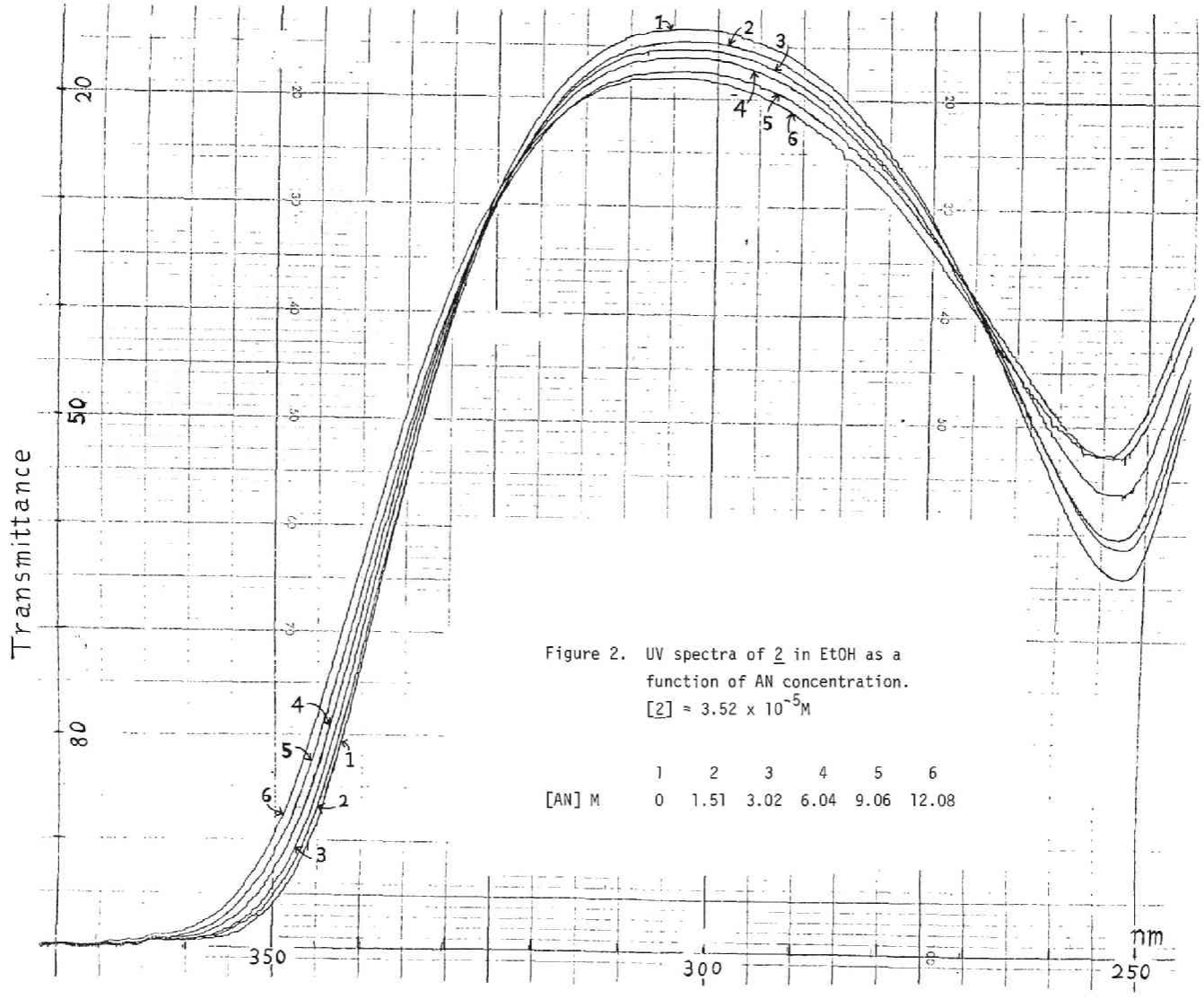


Figure 2. UV spectra of 2 in EtOH as a function of AN concentration. [2] ≈ 3.52 x 10^{-5}M

	1	2	3	4	5	6
[AN] M	0	1.51	3.02	6.04	9.06	12.08

Table 2. Spectral change of imidazoles 1, 2 and 6 by adding acrylonitrile(AN) in ethanol.

Imidazole	Isosbestic Points(nm)		K^a	$\varepsilon_c{}^a$	ε_{Im}	Wavelength taken for calc. (nm)
2-Ph (1)	250	279	0.04 -0.15	9300 -11400	12800	265
2,4,5-TriPh (2)	271	327	0.16 -0.55	18900 -23000	26000	300
1-Me-2,4,5-TriPh (6)	251	293	—	—	24100	275

a) The value of K and ε_c in the case of 6 was unlimited, which may be due to instrumental errors.

Table 3. Wavelengths (molar extinction coefficients) of maximum absorption of imidazoles 2 and 6 in ethanol, acetonitrile and acrylonitrile.

Imidazole	λ_{max} (log ε) nm		
	EtOH (24.3)[a]	MeCN (37.5)[a]	AN (33.0)[a]
2,4,5-TriPh (2)	303 (4.4)	303 (4.4)	308 (4.4)
1-Me-2,4,5-TriPh (6)	283 (4.3)	284 (4.3)	289 (4.4)

a) Dielectric constant (see next chapter).

by AN in ethanol and acetonitrile (Table 4), and the Stern-Volmer plots are shown in Fig. 4. It is clear from these linear plots that the fluorescent state (S_1) of 2 is being quenched in a bimolecular process by AN, in accord with the well-known equation:

$$I_o/I = 1 + k_q\tau[AN] \qquad (1)$$

I and I_o are the quenched and unquenched fluorescence intensities, and k_q and τ are the quenching rate constant and the singlet lifetime in the absence of AN, respectively. Values of $k_q\tau$ in ethanol and acetonitrile are 36 M^{-1} and 46 M^{-1}, respectively.

Quenching of the fluorescence of 2 by AN cannot be due to energy transfer in view of their absorption spectra, but should be due to exciplex formation.[1] Scheme 4 is consistent with eq. (1) where τ is $1 / k_d+k_f$. Im^S and Im^T are S_1 and T_1 states of the imidazoles 2,

Scheme 4

$$Im \xrightarrow{h\nu} Im^S$$

$$Im^S \longrightarrow Im,\ Im^T,\ \text{etc} \qquad k_d$$

$$Im^S \longrightarrow Im + h\nu \qquad k_f$$

$$Im^S + AN \longrightarrow \text{excip. ex} \qquad k_q$$

$$\text{exciplex} \longrightarrow Im + AN \qquad k_{dec}$$

$$\text{exciplex} \longrightarrow \text{products} \qquad k_a$$

respectively. As above-mentioned, exciplex is presumed to be an intermediate in the photoaddition, and Scheme 4 can derive a relationship between photoaddition quantum yield

and AN concentration. The steady-state treatment gives eq. (2).

$$\Phi^{-1} = (1 + k_{dec}/k_a) (1 + 1/k_q\tau[AN]) \qquad (2)$$

Quantum yields for total adduct formation (5 and 13) were measured as a function of AN concentration in acetonitrile, and the results are shown in Table 5 and Fig. 5. From Fig.5 $k_q\tau$ value was estimated to be 35 M^{-1}, which was in fair agreement with that obtained from the fluorescence quenching study. The result suggests that the same mechanism is operative both in the photoaddition and in the fluorescence quenching, and the singlet exciplex is a common intermediate. Similar results were obtained with 6 upon fluorescence quenching and quantum yield measurements and will be described in the next chapter.

It was shown that the ground state complex between 2 and AN does not play at least an important role in the fluorescence quenching and the photoaddition, even if the complex is actually formed. Thus, fluorescence quenching due to the formation of the ground state complex seems negligible under the experimental conditions of Table 4, because the proportion of the complex to the total amount of imidazole 2 is less than 6 % under those conditions, assuming K equal to 0.35. Furthermore, quantum yields for the formation of 5 and 13 changed only 2 times in the experimental range of AN concentration, while the proportion of the ground state complex changed as much as 24 times (Table 5). Actually, the results of fluorescence quenching and quantum yield measurements can be well explained without considering the intermediacy of the ground state complex in Scheme 3.

Solvents affected photoaddition quantum yields and more polar

Table 4. Fluorescence quenching of 2 by AN.

In EtOH ([2]=1.01 x 10^{-6}M)					
[AN] M	0	0.0153	0.0459	0.0918	0.153
I_0/I		1.5	2.7	3.9	7.1
GC (%)[a]		0.5	1.6	3.1	5.1
In MeCN ([2]=9.33 x 10^{-7}M)					
[AN] M	0	0.0153	0.0459	0.0918	0.153
I_0/I		1.7	3.0	5.0	8.5

a) The proportion of the ground state complex to the total amount of 2, assuming K equal to 0.35.

Table 5. Quantum yields of adduct formation (5 and 13) in photoreaction of 2 and AN.

Solvent	MeCN					EtOH	C_6H_6
[AN] M	0.0503	0.101	0.302	1.01	2.01	0.101	0.101
Φ x 10^4	6.1	7.3	8.8	9.3	10	3.0	0.9
GC (%)[a]	1.7	3.4	9.5	26	41		

[2] = 3.45 x 10^{-3} M

a) See the note a) in Table 4.

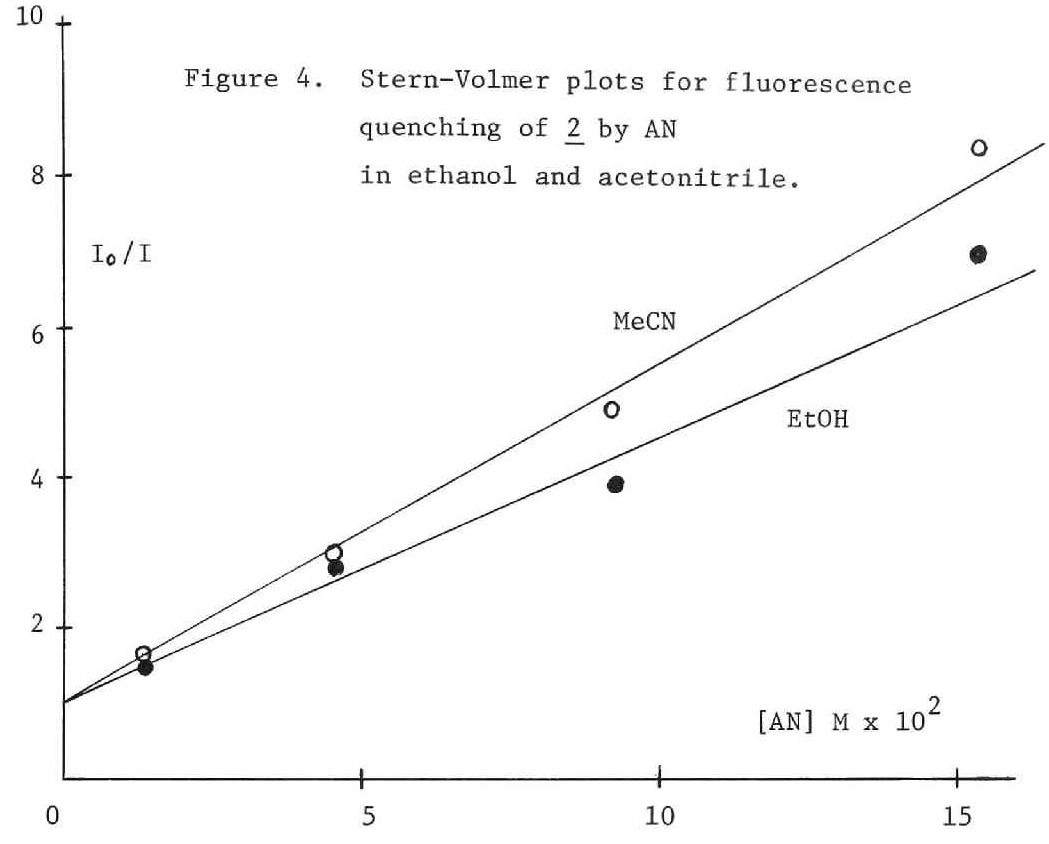


Figure 4. Stern-Volmer plots for fluorescence quenching of 2 by AN in ethanol and acetonitrile.

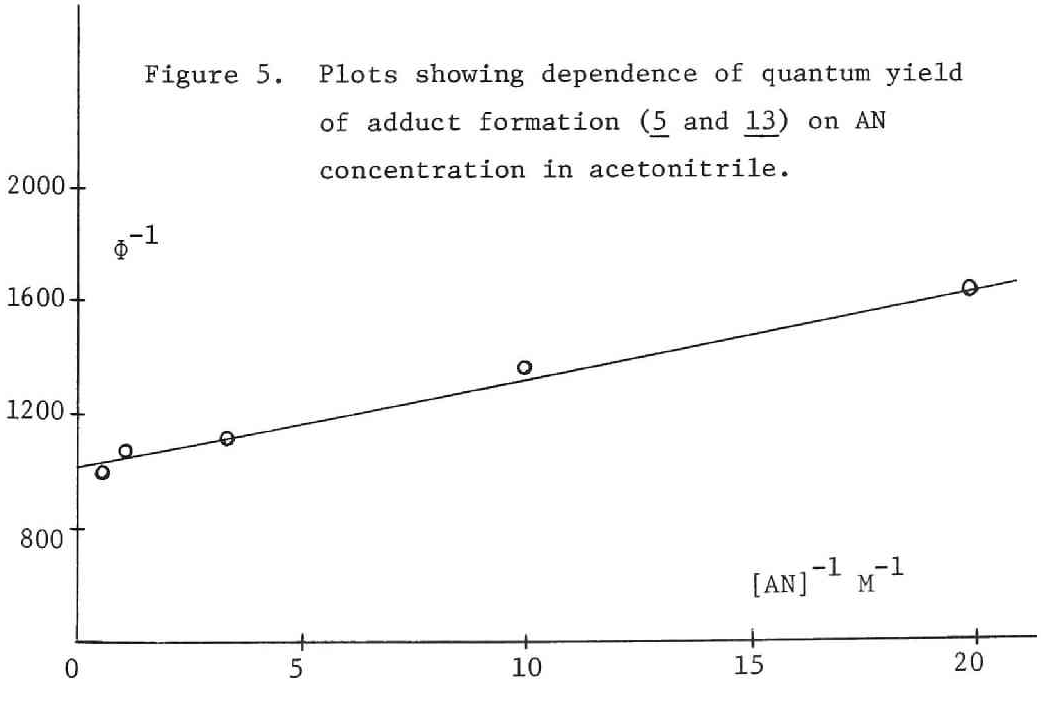


Figure 5. Plots showing dependence of quantum yield of adduct formation (5 and 13) on AN concentration in acetonitrile.

solvent gave higher quantum yields (Table 5). This corroborates the presence of the ion pair 10 as an intermediate for the α-cyanoethylation as McCullough reported in the naphthalene-AN case.

3. Experimental

All melting points are uncorrected. NMR, IR, UV and mass spectra were measured on a Varian EM-360 spectrometer, a JASCO IRA-1 spectrometer, a Shimadzu UV-200 spectrometer and a HITACHI RMU-6C spectrometer, respectively.

Materials.

Ethanol, acetonitrile and acrylonitrile(AN) were distilled prior to use using calcium oxide for ethanol and phosphorous pentoxide for acetonitrile as the drying agents. 2-Phenylimidazole(1) was commercially available and was recrystallized from acetonitrile. 2,4,5-Triphenylimidazole(2),[13] 1-methyl-2,4,5-triphenylimidazole(6)[14] and 1-methyl-2-phenylimidazole(9)[15] were prepared according to the literature methods.

Photoaddition of acrylonitrile(AN) to imidazoles.

Irradiations were carried out with a 450-W (or 400-W) high pressure mercury lamp surrounded by a Pyrex water-cooling jacket under bubbling nitrogen.

(A) 2-Phenylimidazole(1).

(a) In ethanol. A solution of 1 (19.40 g) in AN (150 ml) and ethanol (300 ml) was irradiated for 18 hr with a 450-W lamp. The polymer deposited during irradiation was filtered off and the filtrate was evaporated under reduced pressure. The residue (19.6 g) was then chromatographed on 250 g of silica gel (Mallinckrodt silicic acid 100 mesh). Elution with 3 l of chloroform afforded 330 mg of 2-[2-(2-phenyl-2H-imidazolyl)]propionitrile(4) which was further purified by preparative

TLC (Merck, Kieselgel GF_{254}, chloroform-acetone 15 : 1), VPC (Silicone DC 550, 200°, 2 atm/cm^2 gauge), and finally preparative TLC. Under these VPC conditions 4 changed partly into 1. Further elution with 1 l of chloroform yielded 580 mg of 2-[4(or 5)-(2-phenylimidazolyl)]-propionitrile(3), which was further purified by preparative TLC (chloroform-acetone 10 : 1).

4 : colorless crystals, mp 76-77° (from benzene-petroleum ether) ; ν_{max}(nujol) 2235 (C≡N), 990, 975, 750 and 690 cm^{-1} ; λ_{max}(EtOH) (ε) 240 (1160), 259 (sh. 640), 265 (sh. 590) and 269 nm (sh. 510) ; τ($CDCl_3$) 1.70 (1H, d, J=5.5 Hz, -CH=), 1.72 (1H, d, J=5.5 Hz, -CH=), 2.20-2.77 (5H, m, aromatic H), 6.53 (1H, quar, J=7.5 Hz, -CH-CH_3), and 8.66 (3H, d, J=7.5 Hz, -CH-CH_3); m/e (relative intensity) 197 (M^+, 9) and 143 (M^+-CH_3CHCN, 100). (Found : C, 73.00; H, 5.61; N, 21.34 %. Calcd for $C_{12}H_{11}N_3$: C, 73.07; H, 5.62; N, 21.31 %).

3 : colorless crystals, mp 168.5-169.5°(from 3 : 1 chloroform-carbon tetrachloride) ; ν_{max}(nujol) 2235 (C≡N), 1410, 1145, 790, 710 and 690 cm^{-1} ; λ_{max}(EtOH) 270 nm(ε 12400) ; τ($CDCl_3$)-0.26 (1H, s, disappeared on deuteration, NH), 2.03-2.83 (5H, m, aromatic H), 2.95 (1H, s, -CH=), 6.04 (1H, quart, J=7 Hz, -CH-CH_3) and 8.37 (3H, d, J=7 Hz) ; m/e (relative intensity) 197 (M^+, 76) and 182 (M^+-CH_3, 100). (Found : C, 72.81; H, 5.37; N, 21.37 %. Calcd for $C_{12}H_{11}N_3$: C, 73.07; H, 5.62; N, 21.31 %). Further elution with chloroform, chloroform-acetone and acetone recovered 1 (96 %).

(b) In acetonitrile. A solution containing 11.12 g of 1 in AN (150 ml) and acetonitrile (350 ml) was irradiated for 79 hr with a 400-W lamp. After similar work-up of the photolysate (silica gel, 200 g), 250 mg of 4, 310 mg of 3 and 9.49 g of recovered 1 were isolated.

(B) 2,4,5-Triphenylimidazole (2).

(a) In ethanol. A solution of 2 (1.53 g) in AN (70 ml) and ethanol (350 ml) was irradiated with a 400-W lamp for 3.5 hr. After removal of the polymer deposited and the solvent as described above, the residue was chromatographed on 50 g of silica gel. Elution with

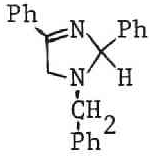
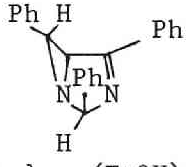
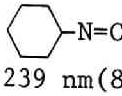
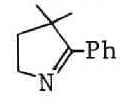
1400 ml of benzene afforded 340 mg of pure 2-[2-(2,4,5-triphenyl-2H-imidazolyl)]propionitrile(5) and subsequently 370 mg of a mixture of 5 and an unidentified product 13 (5 : 13 = 0.75 : 0.25 by NMR). The latter compound appeared to be a 1 : 1 adduct similar to 5 judging from the NMR spectrum of the mixture (NMR signals at $\tau(CDCl_3)$ 6.05 (1H, quar, J=7.5 Hz) and 9.01 (3H, d, J=7.5 Hz) are attributable to the α-cyanoethyl group of 13) and the photochemical conversion of 5 into 13 (vide infra). Attempts to isolate 13 by chromatographic methods were unsuccessful. 5 : colorless crystals, mp 218.5-219° (from benzene-petroleum ether) ; ν_{max}(nujol) 2235 (C≡N), 1550, 1490, 1020, 770, 760, 700 and 690 cm^{-1}. The spectrum at the region 1625-1475 cm^{-1} is very similar to that of 2,2,4,5-tetraphenyl-2H-imidazole.[12] λ_{max}(EtOH) 266 nm (ε 7500) which is similar to that of 2,2-dimethyl-4,5-diphenyl-2H-imidazole (262 nm (ε 9700)).[10] $\tau(CDCl_3)$ 1.93-2.77 (15H, m, aromatic H), 6.34 (1H, quar, J=7.5 Hz, -C<u>H</u>-CH_3), 8.56 (3H, d, J=7.5 Hz, -CH-C<u>H</u>$_3$). (Found : C, 82.71; H, 5.59; N, 11.79 %. Calcd for $C_{24}H_{19}N_3$: C, 82.49; H, 5.48; N, 12.03 %). Further elution with benzene (800 ml) afforded a complex mixture (280 mg) which was difficult to separate. Recovered 2 (420 mg) was then eluted with chloroform (600 ml).

(b) In acetonitrile. The photolysate (450-W lamp, 4 hr) from 2 (530 mg) in AN (50 ml) and acetonitrile (350 ml) was filtered to remove the AN polymer. The filtrate was evaporated under reduced pressure, taken up in hot chloroform (ca. 200 ml), filtered again to remove the insoluble polymeric material, and finally evaporated under reduced pressure. The residue was chromatographed on 30 g of silica gel. Pure 5 (240 mg) was eluted with benzene (1500 ml). Product 13 was not detected, although in other similar runs it was detected. Elution with chloroform (1000 ml) afforded a complex mixture (300 mg) which was difficult to separate. Recovered 2 was not detected in any fraction.

(C) 1-Methyl-2,4,5-triphenylimidazole (6).

(a) In ethanol. The photolysate (400-W lamp, 4 hr) from 6 (2.64 g) in AN (150 ml) and ethanol (250 ml) was filtered. The filtrate was

evaporated under reduced pressure , and the residue was chromatographed on 100 g of silica gel. After elution of a small amount (150 mg) of low-polarity products with benzene (800 ml), 2.03 g of recovered 6 which contained a small amount of cis- and trans-1,2-dicyanocyclobutanes as impurities (NMR) was eluted with chloroform (900 ml). Further elution with chloroform (700 ml) followed by repeated preparative TLC (3 : 1 benzene-ethyl acetate) of the eluate yielded 2,4-diazabicyclo[3,2,0]hept-2-enes, 7a (less polar,510 mg) and 7b (more polar, 30 mg) which were contaminated with a small amount of cis- and trans-1,2-dicyanocyclobutanes (NMR). Pure 7a and 7b which were free from the cyclobutanes were obtained by recrystallization.

7a : colorless crystals, mp 158-162° (from benzene-petroleum ether); ν_{max}(nujol) 2230 (C≡N), 1590, 1565, 1500, 1060, 760, 715 and 690 cm^{-1}; λ_{max}(EtOH)(ε) 222 (sh, 18300) and 266 nm (2500) which are consistent with the 2-phenyl-2-imidazoline structure [1-methyl-2-phenyl-2-imidazoline[16] : λ_{max}(EtOH)(ε) 223 (9400) and 264 nm (2500). 2-phenyl-2-imidazoline[16] : λ_{max}(EtOH)(ε) 224 (12400) and 267 nm(2800). cis-2,4,5-triphenyl-2-imidazoline[16] : λ_{max}(EtOH)(ε) 224 (18800) and 268 nm (6200).] but not with the 3-imidazoline or Schiff base structures [15 : λ_{max} (95 % EtOH)(ε) 245 nm (12500)[17a].  : λ_{max}(MeOH)(ε) 247 nm (12400)[17b].  : λ_{max}(95 % EtOH)(ε) 245 nm (20000)[17b]. $PhCH_2$-N=CHPh : λ_{max}(EtOH)(ε) 250 (20800) and 280 nm (sh, 2080).[17c] n-Bu-N=CH-Ph : λ_{max}(EtOH)(ε) 246 (14500), 280 (1520) and 288nm (1000).[17d]  -N=CMePh : λ_{max}(EtOH)(ε) 240 (10000).[17d]  -Ph : λ_{max}(EtOH)(ε) 239 nm(8900).[17d]] ;

τ($CDCl_3$) 2.03-3.13 (15H, m, aromatic H), 5.97-7.16 (3H, ABC pattern, J_{AB}=12 Hz, J_{BC}=5 Hz, J_{AC}=10 Hz, $-CH_AH_B-CH_C-$) and 7.33 (3H, s, $-N-CH_3$); m/e (relative intensity) 363 (M^+, 0.1) and 310 (M^+-CH_2CHCN, 100).

(Found : C, 82.85; H, 5.73; N, 11.42 %. Calcd for $C_{25}H_{21}N_3$: C, 82.61; H, 5.82; N, 11.56 %.)

7b : colorless crystals, mp 197-200° (from aqueous methanol) ; ν_{max}^{nujol} 2230 (C≡N), 1590, 1570, 1500, 1065, 765, 710 and 695cm^{-1} ; $\lambda_{max}^{EtOH}(\varepsilon)$ 222 (sh, 16800) and 266 nm (3000) ; $\tau(CDCl_3)$ 2.20-3.23 (15 H, m, aromatic H), 6.05-6.86 (3H, ABC pattern,-CH_2-CH-) and 7.40 (3H, s, -N-CH_3) ; m/e (relative intensity) 363 (M^+, 0.5) and 310 (M^+-CH_2CHCN, 100). (Found : C, 82.13; H, 5.87; N, 11.32 %. Calcd for $C_{25}H_{21}N_3$: C, 82.61; H, 5.82; N, 11.56 %). Even a trace of 8 could not be detected.

(b) In acetonitrile. The photolysate (400-W lamp, 9 hr) from 2.07 g of 6 in AN (100 ml) and acetonitrile (150 ml) was treated in the same manner as described in (B)-(b). The residue (3.99 g) was chromatographed on 80 g of silica gel. Elution with 800 ml of a mixture of 2 : 1 benzene-chloroform, followed by preparative TLC (2 : 1 chloroform-benzene), afforded 340 mg of 1-methyl-2,4,4-triphenyl-Δ^2-imidazolin-5-one(8), mp 172.5-174° (Lit.[14] 165°), and 660 mg of recovered 6. The identity of 8 was confirmed by direct comparison (NMR and IR) with an authentic sample.[14] Further elution with the same solvent (800 ml) followed by preparative TLC (10 : 1 benzene-ethyl acetate), gave 270 mg of additional recovered 6 and 700 mg of cis- and trans-1,2-dicyanocyclobutanes (oil, mainly cis isomer[18]). Further elution with the mixture of 1 : 4 benzene-chloroform (600 ml) yielded 210 mg of additional recovered 6 and 850 mg of cis- and trans-1,2-dicyanocyclobutanes (solidified on standing, mainly trans isomer[18]). The identity of the cyclobutanes was confirmed by comparison with an authentic sample (commercially available). Even traces of 7a and 7b could not be detected.

(D) 1-Methyl-2-phenylimidazole (9).

(a) In ethanol. The photolysate (450-W lamp, 21 hr) from 9 (0 98 g) in AN (50 ml) and ethanol (180 ml) was filtered. The filtrate was evaporated and separated by preparative TLC (1 : 1 chloroform-acetone). Recovered 9 (835 mg) and a small amount of cis- and trans-1,2-dicyanocyclobutanes (10 mg) were isolated, but yields of photoadducts between

AN and 9 were estimated to be below o.5 % by NMR analysis, even if they were produced.

(b) In acetonitrile. A Pyrex tube containing a solution of 9 (110 mg) in AN (5 ml) and acetonitrile (15 ml) was irradiated externally with a 400-W lamp under bubbling nitrogen for 7.5 hr, but essentially no products from 9 was observed by the NMR and TLC analyses of the photolysate, although polymerization of AN occurred as usual.

Chemical reactions of photoproducts.

(A) 2-[2-(2-Phenyl-2H-imidazolyl)]propionitrile (4).

i) Hydrolysis. A solution of 4 (92 mg) in ethanol (1 ml) was heated with 3 ml of dilute hydrochloric acid (6 %) on a water bath (∿100°) for 4 hr. The mixture was extracted three times with 10 ml of ether and the combined ethereal extracts were evaporated under reduced pressure after drying over sodium sulfate. The residue (82 mg) was shown to be almost pure 2-benzoylpropionitrile from its TLC analysis and the identity was confirmed by direct comparison (NMR, IR) with an authentic sample.[19]

ii) Photolysis. A Pyrex tube containing a solutioq of 4 (140 mg) in ethanol(40 ml) was sealed with a glass-stopper after bubbling nitrogen and irradiated externally with a 400-W high pressure mercury lamp surrounded by a Pyrex cooling jacket for 14 hr. After removal of the solvent, the residue was subjected to preparative TLC (15 : 1 chloroform-acetone) to give 22 mg of 1 and 93 mg of recovered 4, but even a trace of 3 was not detected (TLC).

Under the same photolysis conditions, 3 was stable (TLC).

iii) Reaction with $LiAlH_4$. A solution of 4 (52 mg) in absolute ether (5 ml) was heated with 20 mg of $LiAlH_4$ under reflux for 2.5 hr. The mixture was treated with water (1 ml) and then with aqueous sodium hydroxide (80 mg in 2 ml water) and extracted with 10 ml of ether three times. The ethereal extracts were separated by preparative TLC (5 : 1 chloroform-acetone) to yield 17 mg of 1.

iv) Thermolysis. A solution of 4 (41 mg) in cumene (5 ml) was

heated under reflux for 36 hr. The reaction mixture was separated by preparative TLC (20 : 1 chloroform-acetone). Besides recovered 4 (30 mg), bicumy (mp 120.5-122°(Lit.[20] 115°)), which gave satisfactory NMR and IR spectra, was the only identifiable product. The decomposition of 4 into 1 during VPC was already described.

(B) 2-[2-(2,4,5-triphenyl-2H-imidazolyl)]propionitrile (5).

i) Hydrolysis. A mixture of 5 (316 mg) and sulfuric acid (75 %, 974 mg) was heated on a water bath (∿100°) for 1 hr and then 10 ml of water was added. The mixture was extracted with ether three times (total 80 ml) and the ethereal extracts were separated by preparative TLC (chloroform) to yield 166 mg of benzil (mp 98-99°, Lit.[21] 95°) which is identical with an authentic sample (NMR, IR) and 76 mg of 2-benzoylpropionamide (mp 155-156°, Lit.[22] 150-152°) which gave satisfactory NMR, IR, mass and analytical data.

ii) Photolysis. A Pyrex tube containing a solution of 5 (62 mg) in acetonitrile (25 ml) was irradiated in the same manner as (A) - ii) for 12 hr, and the photolysate was separated by preparative TLC (50 : 1 chloroform-acetone) to afford 24 mg of 2 and 2 mg of recovered 5. When the irradiation was stopped after a few hours, the formation of 13 was observed by NMR analysis.

iii) Reaction with $LiAlH_4$. A mixture of 5 (513 mg) and $LiAlH_4$ (110 mg) in tetrahydrofuran (40 ml) was heated under reflux for 4 hr. The reaction mixture was treated with water (ca. 5 ml), then with hydrochloric acid (ca. 0.5 ml) and extracted with ether (total 150 ml). After evaporation of the ether extracts, the residue was recrystallized from chloroform-acetone to afford 203 mg of 2. From the mother liquor additional 2 (150 mg) was isolated by preparative TLC (30 : 1 chloroform-acetone).

iv) Thermolysis. A solution of 5 (31 mg) in cumene (5 ml) was heated under reflux for 12 hr, and the reaction mixture was separated by preparative TLC (50 : 1 chloroform-acetone) to afford 25 mg of recovered 5 and 5 mg of 2.

(C) Thermolysis of 7a.

A solution of 7a (16 mg) in cumene (2 ml) was heated under reflux for 4 hr and the reaction mixture was separated by preparative TLC (50 : 1 chloroform -acetone) to give 11 mg of 6 and a trace of 7a.

(D) $LiAlH_4$ reduction of 8.

A mixture of 8 (129 mg) and $LiAlH_4$ (12 mg) in absolute ether (20 ml) was heated under reflux for 3 hr. The reaction mixture was treated with water (2 ml), filtered to remove some insoluble solid, and evaporated. The residue was separated by preparative TLC (20 : 1 chloroform-methanol) to give 63 mg of recovered 8 and 25 mg (38 %) of 5-hydroxy-1-methyl-2,4,4-triphenyl-Δ^2-imidazoline(14). 14 : colorless crystals, mp >195°(decomp.) (from acetone-methanol); ν_{max}(nujol) 1595, 1570, 1120, 1065, 705 and 690 cm^{-1} ; λ_{max}(EtOH)(ε) 222 (7030) and 260 (sh, 1790) ; τ($CDCl_3$(1)-CD_3OD(1)) 2.23-2.84 (15H, m, arom), 4.27 (1H, s, C<u>H</u>-O), 5.43 (1H, s, disappeared on deuteration, O<u>H</u>), 7.03 (3H, s, $C\underline{H}_3$); m/e (relative intensity) 328 (M^+,3), 310 (M^+-H_2O, 100) and 269 ([Ph-C(=N)-C(Ph)-Ph]$^+$, 40). (Found : C, 80.07; H, 6.13; N, 8.27 %. Calcd. for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53 %).

UV measurements.

The measurements were repeated several times to obtain the correct isosbestic points and the absorbance used for calculation of K and ε_c.

Fluorescence quenching.

The fluorescence intensities for solutions of 2 containing various amounts of AN were measured at room temperature on a Shimadzu MPS-50L with irradiation at 290 nm. The intensity ratios I_o/I were calculated at wavelengths of the maximal emission (399 nm in ethanol and 401 nm in acetonitrile). No special care was taken for deaeration of solutions.

Quantum yield measurements.

Pyrex tubes containing a solution of 2 (15.3 mg) were sealed with glass-stoppers after bubbling nitrogen and adding quickly a known volume of AN. The total volume of each solution was adjusted to 15 ml by adding the solvent. They were photolyzed for 1.5 hr on a

merry-go-round apparatus using a 400-W high pressure mercury lamp with continuous flow of a cooled pottasium chromate-pottasium carbonate solution[23] through a Pyrex cooling-jacket . Light intensities were measured by ferrioxalate actinometry.[24] (I_o^i = 6.7 x 10^{17} quanta/sec). Products 5 and 13 were assayed by TLC analysis (benzil as the internal standard, 1 : 3 benzene-chloroform) using a Shimadzu TLC Scanner CS-900. The irradiations were stopped at less than 5 % conversion.

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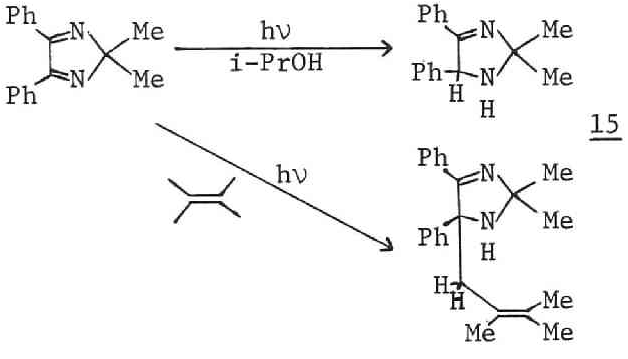

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C H A P T E R II

The Photochemical Reaction of Tetra-substituted Imidazoles with α,β-Unsaturated Nitriles. The Dual Pathways via an Exciplex and a Dissociated Ion Pair.

Tetra-substituted imidazoles 1, 8 and 12 react photochemically with acrylonitrile to afford cycloadducts 3, 10 and 13, respectively, in solvents having medium or low polarity, whereas 1 and 8 gave Δ^2-imidazolin-5-ones 2 and 9, respectively, in highly polar solvents (Table 1). The presence of singlet exciplex intermediates was demonstrated from fluorescence quenching studies and quantum yield measurements. Thus, the solvent effects are well explained by change of the exciplex structure with solvent polarity, that is, by exciplex and radical ion pair formation (Scheme 1). Such electron transfer mechanism can also well explain the difference in reactivity among acrylonitrile, methacrylonitrile and crotononitrile, and the formation of 6 and benzil in the photolysis of 1 and acrylonitrile in methanol. A labelling experiment with $H_2{}^{18}O$ is consistent with the route to lead to Δ^2-imidazolin-5-one depicted in Scheme 1.

In addition, the photoaddition of acrylonitrile to oxazole 20 and thiazole 21 was studied for comparison (Table 4).

1. Introduction

In the preceding chapter[2] the author has shown the striking solvent effect that the irradiation of 1-methyl-2,4,5-triphenylimidazole (1) in the presence of acrylonitrile (AN) led to the formation of 1:1 cycloadducts 3a and 3b in ethanol, while in acetonitrile a Δ^2-imidazolin-5-one 2 was formed. The author now wishes to propose the mechanisms for these reactions (Scheme 1). The keystep is the formation of an exciplex and/or a dissociated ion pair. The photochemical reaction of 1 with AN is important in view of the current interest in the effect of solvent polarity on the fate of exciplexes.[1]

2. Results and Discussion

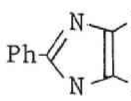
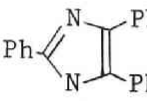
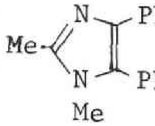
In all preparative runs imidazoles 1, 8 and 12 were irradiated through Pyrex in the presence of a large excess of acrylonitrile (AN). After removing the AN polymer by filtration, crude photoproducts were separated by chromatographic methods to give Δ^2-imidazolin-5-ones (2 and 9), cycloadducts (3, 10 and 13), phenanthrene derivatives (4, 11 and 14) and others (Table 1). Like 1-methyl-2,4,5-triphenylimidazole(1) (No 1,No 8), 1,2,4,5-tetraphenylimidazole(8) afforded cycloadducts (10a and 10b) in ethanol (No 15) and a Δ^2-imidazolin-5-one 9 in acetonitrile (No 14). However, 1,2-dimethyl-4,5-diphenylimidazole(12) gave no Δ^2-imidazolin-5-one in acetonitrile (No 16), although cycloadducts (13a and 13b) were similarly formed in ethanol (No 17). Obviously the formation of phenanthrene derivatives 4,11 and 14 is competing with that of the

imidazolinones and cycloadducts. In fact, better yields of 4 (No 4, No 9, No 13) and 11[3] were obtained by the irradiation of 1 and 8, respectively, in the absence of AN. The [2+2] adduct structure of 10 and 13 was assigned from their spectral properties.

The solvent effect on these reactions was studied in detail for imidazole 1 (Table 1, No 1 - No 13). It is notable that imidazolinone 2 has a tendency to become a main product in solvents having a high dielectric constant (acetonitrile, acrylonitrile and methanol), whereas in solvents of a medium or low dielectric constant (ethanol, 2-propanol and benzene) cycloadducts 3a and 3b are formed predominantly. It is also notable that benzil and 6 could be isolated besides 2 and 3 in methanol. The structure 6 was tentatively assigned from its spectral data, but it is certain that 6 is an adduct between 1 and two AN molecules and has a α-cyanoethyl group. On hydrolysis with dilute hydrochloric acid 6 gave α-bezoylpropionitrile(71%) and benzil(33%). The role of water in the formation of 2 is complex. Undoubtedly the oxygen atom of 2 would be derived from water which is present in solvents as impurity. However, even when water was added externally (No 3, No 5, No 12 and ^{18}O incorporation experiment), the yield of 2 did not increase and the material balance of the reaction became considerably worse (No 3, No 5).

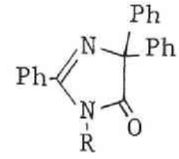
In the preceding chapter[2] the presence of singlet exciplexes as intermediates in the α-cyanoethylation of N-unsubstituted imidazoles with AN was suggested based on fluorescence quenching studies and quantum yield measurements. The same experiments done with 1 has likewise indicated the intermediacy of a singlet exciplex in the formation of imidazolinone 2. Thus, the fluorescence emission of 1 was quenched by

Table 1. Photochemical reaction of imidazoles (Im) and

No	Imidazole	Mx10^2	Mole ratio of AN/Im	Solvent (ε)[b]	Irradn. time (hr)	Products (%)[a] Imidazolinones	Cycloadducts
						2	3a+3b
1		2.67	220	MeCN (37.5)	9	16	0
2		1.03	3.6	MeCN	9, S[c]	5	0
3		1.85	200	MeCN-H_2O (2:1)	10, N[c]	6	2
4		1.78	0[d]	MeCN	21.5, S[c]	0	—
5		1.58	240	MeOH-H_2O (10:1) (36.8)	11, N[c]	5	12
	1						
6		1.40	1070	CH_2=CH-CN (33.0)	11, N[c]	6	0
7		2.48	190	MeOH (32.6)	15	3	6
8		2.13	270	EtOH (24.3)	4	0	18
9		1.35	0[d]	EtOH	21.5, S[c]	0	—
10		1.66	230	i-PrOH (18.3)	11, N[c]	4	54
11		1.69	230	C_6H_6 (2.2)	13.5, N[c]	trace	27
12		1.50	250	C_6H_6-H_2O (300:1)	10, N[c]	3	22
13		1.68	0[d]	C_6H_6	22.5, S[c]	0	—
						9	10a 10b
14		0.749	290	MeCN	3	6	0 0
15		0.823	550	EtOH	6	0	13 5
	8						
							13a 13b
16		1.16	190	MeCN	7	—	0 0
17		1.15	190	EtOH	9.5	—	39 3
	12						

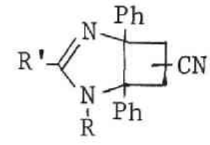
acrylonitrile (AN) in various solvents.

Products (%)[a]		Recovered Im (%)
Phenanthrene derivatives	Others	
4		
0	**5**	55
33	**5**	44
0	**5**, f	12
17	—	70
0	**6** + Benzil (<12 %)	43
0	—	73
0	**6**(4 %), **7a** Benzil(6 %)	65
0	**5**	77[e]
10	—	76
trace	**5**	27
0	**5**	44
0	**5**, f	47
4	—	90
11		
9	**5**	43
0	**5**	54
14		
13	**5**	49
0	**7b**	36



2; R=Me

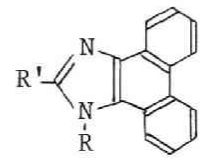
9; R=Ph



3; R=Me, R'=Ph

10; R=R'=Ph

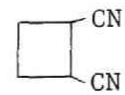
13; R=R'=Me



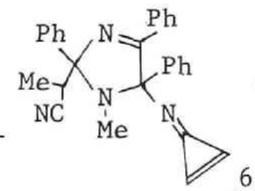
4; R=Me, R'=Ph

11; R=R'=Ph

14; R=R'=Me

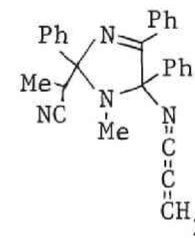


5 (a mixture of cis and trans-isomers)



6

or



$ROCH_2CH_2CN$

7a; R=Me

7b; R=Et

Table 1. (continued)

a) Calculated based on the initial amount of imidazoles.

b) ε : dielectric constant.
MeOH-H_2O (10:1) : R. H. Young, K. Wehrly and R. L. Martin, J. Amer. Chem. Soc., 93, 5774 (1971).
CH_2=CHCN : W. Dannhauser and A. F. Flueckinger, J. Phys. Chem., 68, 1814 (1964).
Other data were taken from "Yoobai Kooka" M. Seo and K. Arai, Sangyo Tosho, p 68 (1970).

c) Externally irradiated in a closed Pyrex tube (S) or under bubbling nitrogen (N).

d) Irradiated in the absence of AN.

e) Contained a small amount of 5.

f) Even if benzil and 6 were actually formed, they seem to exist only in trace amounts (TLC).

AN in acetonitrile, showing linear Stern-Volmer plots with $k_q\tau$ value of 13 M^{-1}(Figure 1),which was almost equal to that (17 M^{-1}) obtained from quantum yield measurements for the formation of 2 in acetonitrile as a function of AN concentration (Figure 2 and Table 5). In ethanol, the fluorescence of 1 was also quenched by AN ($k_q\tau$= 6 M^{-1}, Figure 1), but quantum yield measurements for the formation of 3 in ethanol were unsuccessful due to the efficient formation of AN polymers which deposited as a white solid during the photolysis. However, it seems reasonable to assume a siglet exciplex responsible for the formation of 3 as well as 2. In fact, [2+2] photocycloadditions have often been interpreted as involving prior formation of singlet exciplexes[4].

Considering that the cyano group of AN appears to function directly in the formation of imidazolinones, the photochemical reaction of other nitriles with 1 was examined. As shown in Table 2, only methacrylonitrile was effective to cause the formation of 2. In sharp contrast, crotononitrile was ineffective. Benzonitrile and 2-cyanopyridine were also ineffective. The results with the latter nitrile will be discussed in the next chapter. It must be mentioned that AN causes the formation of imidazolinone 2 more readily than methacrylonitrile in acetonitrile. As a matter of fact, a large quantity of 4 was concurrently produced in the case of methacrylonitrile, which may indicate that the interaction of methacrylonitrile with the excited 1 is weaker than that of AN.

These facts (the solvent effects, the intermediacy of singlet exciplexes, and the difference in reactivity among AN, methacrylonitrile and crotononitrile) can be well rationalized by Scheme 1, which also

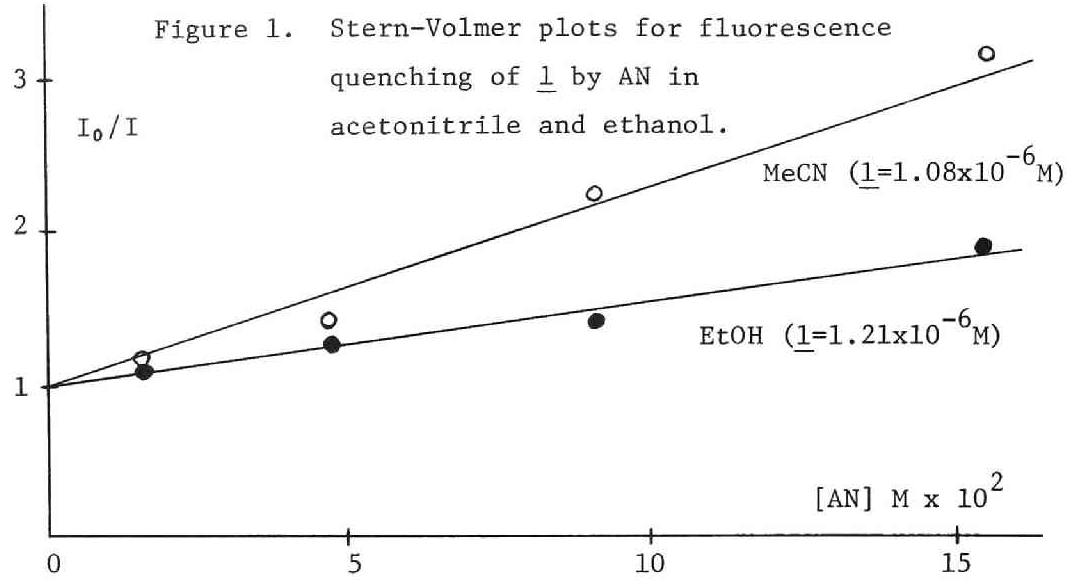


Figure 1. Stern-Volmer plots for fluorescence quenching of $\underline{1}$ by AN in acetonitrile and ethanol.

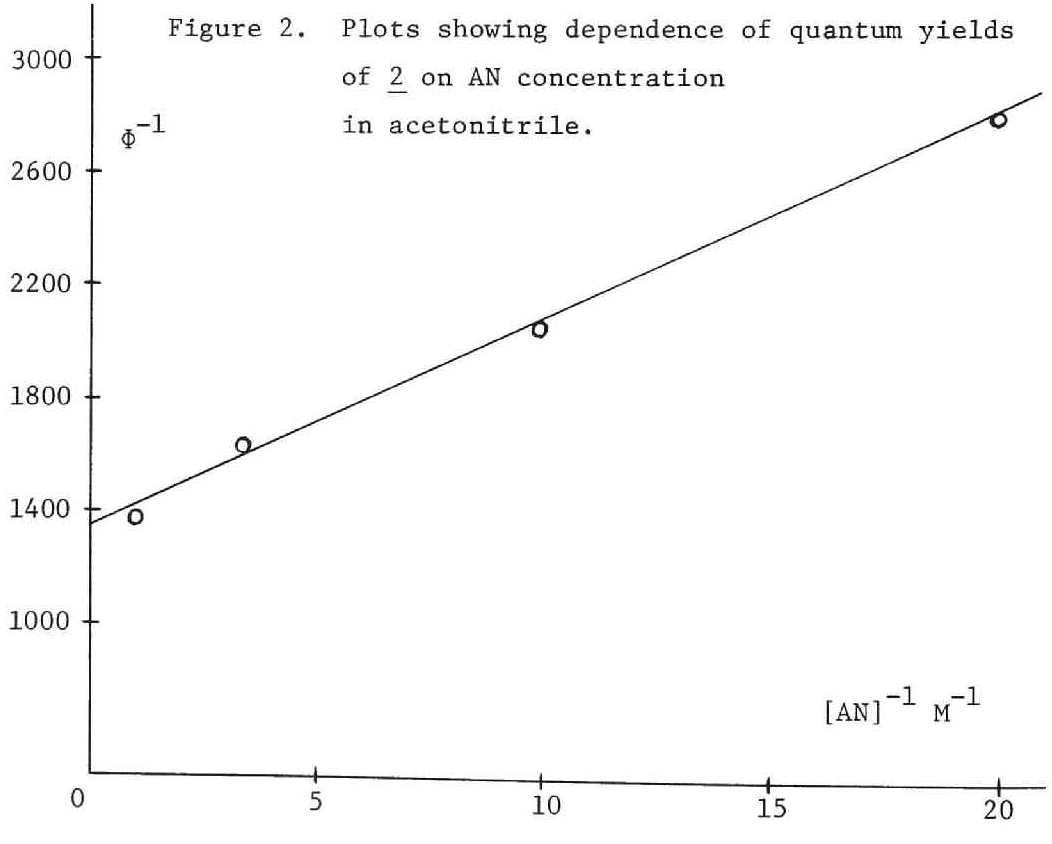
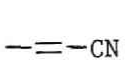
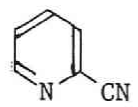
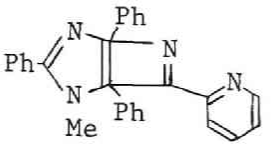


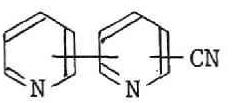
Figure 2. Plots showing dependence of quantum yields of $\underline{2}$ on AN concentration in acetonitrile.

Table 2. Photochemical reactions of 1 with various nitriles.

Nitrile	M of 1 x10^2	Mole ratio of Nitrile/1	Solvent	Irradn. time (hr)	Products(%)[c] 2	4	Others			Recovered(%) Im	Nitrile
	1.10	180	MeCN	9	6	72	—			7	—
	1.09	180	EtOH	9	a	a	Benzil(17)			a	—
	1.01	240	MeCN	13.5[b]	0	22	—			78	—
	1.26	200	EtOH	13.5[b]	0	34	—			50	—
PhCN	1.52	32	MeCN	23[b]	0	39	—			58	—
	1.52	32	EtOH	23[b]	0	31	—			51	—
							27	28[d]	29[d]		
	0.996	4.2	MeCN	13	0	19	48	40	4	4	37
	1.33	4.4	MeCN	27	0	3	52	35	—	0	33
	1.34	4.3	EtOH	27	0	11	7	3	—	69	88



27



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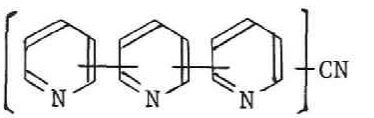

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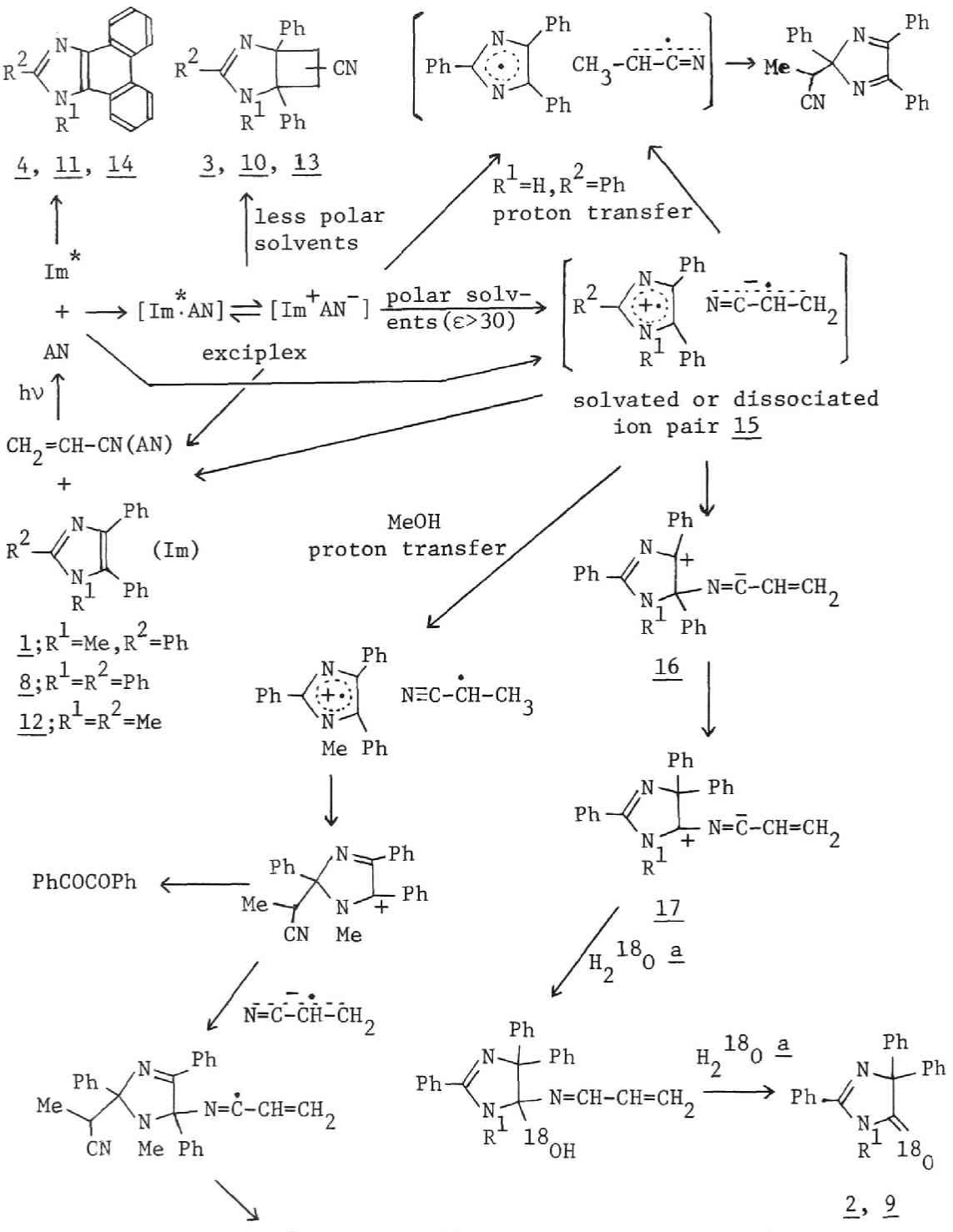
a) The products were detected but isolation of these products were unsuccessful, as large amounts of methacrylonitrile polymers were produced.

b) Externally irradiated in a closed Pyrex tube (S).

c) Yields are based on imidazole 1 used, unless otherwise noted.

d) Based on 2-cyanopyridine used.

Scheme 1


4, 11, 14
3, 10, 13
less polar solvents
R1=H, R2=Ph proton transfer
Im*
+ AN
hν
CH2=CH-CN(AN)
+
[Im*·AN] ⇌ [Im+AN−]
polar solvents (ε>30)
exciplex
solvated or dissociated ion pair 15
(Im)
1; R1=Me, R2=Ph
8; R1=R2=Ph
12; R1=R2=Me
MeOH proton transfer
16
17
PhCOCOPh
H2 18O a
6
2, 9
a Water is contained in solvents as impurity.

includes the mechanism for the α-cyanoethylation of lophine described in the preceding chapter.[2] According to this scheme, the lowest singlet excited imidazole interacts with AN to form an exciplex or to form a solvated (dissociated) ion pair directly or *via* the exciplex. Cycloadducts 3, 10 and 13 are formed *via* an exciplex in solvents of relatively low polarity. Imidazolinones 2 and 9 are formed *via* a solvated or dissociated ion pair in highly polar solvents ($\varepsilon>30$ except isopropyl alcohol). Such change of the exciplex structure with solvent polarity[5] and the solvent dependence of product distribution[1,6] are well-known (Scheme 2). The intermediacy of a dissociated radical ion pair has been shown or postulated for the photoreaction of a number of donor-acceptor systems.[6,7] Weller, et al.[5a] have shown that donor-acceptor systems which lead to exciplexes in non-polar solvents lead, however, in polar solvents to the competitive formation of solvated ion pairs through electron transfer, and that in highly polar solvents ($\varepsilon>30$) the latter process predominates. When the 1-nitrogen of imidazoles is unsubstituted, proton transfer and subsequent radical coupling reaction resulting in α-cyanoethylation occur from either an exciplex of strong charge-transfer character, a solvated (dissociated) ion pair 15 or both.[2]

The relative facility for the nitrile to effect the formation of 2 in acetonitrile (CH_2=CHCN > CH_2=CMeCN > MeCH=CHCN as mentioned above) is consistent with the order of the values of their half-wave potentials ($E_{1/2}$, Table 3), supporting the intermediary formation of radical ion pair 15. The different behavior between methacrylo-

nitrile and crotononitrile may also be attributed to a difference in the stability of intermediate 16, seeing that the corresponding intermediate 18a from

Scheme 2. Examples of dichotomous photoproducts via an exciplex in nonpolar solvents and a dissociated ion pair in polar solvents.

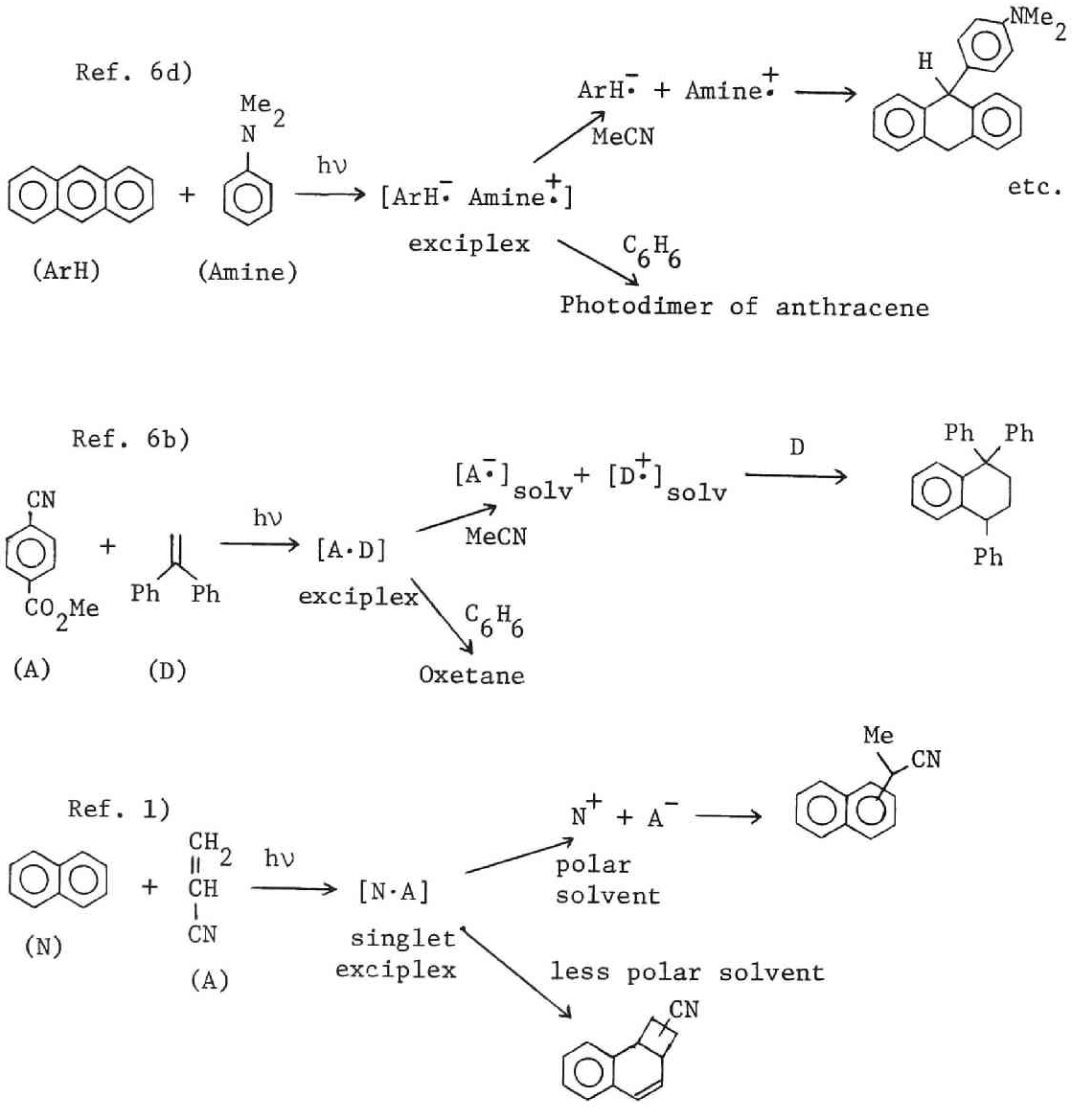


Table 3. Half-wave potentials of polarograms of nitriles.

Nitrile	$E_{1/2}$(V)	
CH_2=CHCN	1.67[a]	
CH_2=CMeCN	1.79[a]	-2.07[b]
MeCH=CHCN	1.91[a]	-2.37[c]
Benzonitrile		-2.69[d]
2-Cyanopyridine		-0.4~-2.0[e]

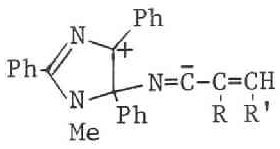
a) I. G. Sevast'yanova and A. P. Tomilov, Zh. Obshch. Khim., 33, 2815 (1963), Chem. Abstr., 60, 1583e (1964). (0.1 M Et_4NI in DMF, vs. the Hg layer in the bottom of the cell)

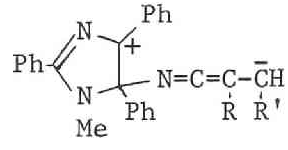
b) "Kagaku Binran" Kisohen II, Ed. Nippon Kagakukai, Pub. Maruzen, p 1383 (1966). (0.1 M Me_4NBr, vs. SCE)

c) H. O. House, L. E. Huber and M. J. Umen, J. Amer. Chem. Soc., 94, 8471 (1972). (0.50 M n-Bu_4NBF_4 in DMF, vs. SCE)

d) G. Anthoine, J. Nasielski and B. Wilmet-Devos, Bull. Soc. Chim. Belg., 78, 465 (1969), Chem. Abstr., 72, 50345y (1970). (in DMF)

e) A. M. Kardos, P. Valenta and J. Volke, J. Electroanal. Chem., 12, 84 (1966). (pH 6.4, vs. saturated MSE)





18a; R=H, R'=Me
b; R=Me, R'=H

crotononitrile is less stable than 18b from methacrylonitrile on account of the electron-donating effect of methyl group. The intermediacy of nitrile ylide 17 and the subsequent participation of water are the most probable pathway for the formation of 2.# This is supported by a tracer experiment which showed the almost quantitative incorporation (91 % by mass spectroscopic analysis) of ^{18}O into 2 on irradiation in the presence of ^{18}O-enriched water in acetonitrile. The addition of water to 17 in the direction depicted in Scheme 1 is consistent with

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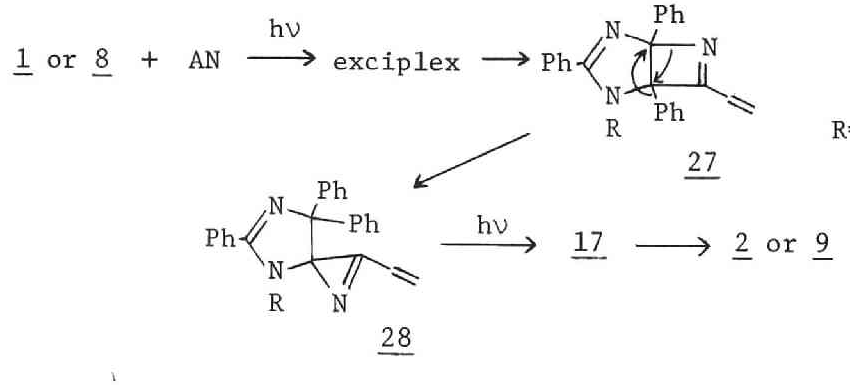
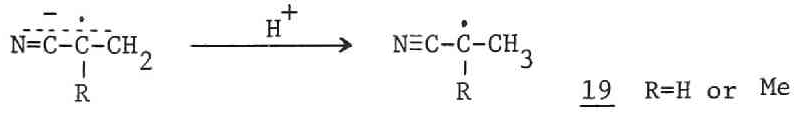
Taking into consideration the photochemical addition of 1 to 2-cyanopyridine described in the next chapter, the formation of the imidazolinone 2 or 9 through cycloaddition between the C_4-C_5 double bond of imidazole 1 or 8 and the cyano group of AN may be possible as is shown in the scheme below. However, while the mechanism described in Scheme 1 has many supports (see text), the mechanism shown below seems to be rather lacking in evidence. Indeed, there is no preceding example, I think, of the skeletal rearrangement of an azetine to an azirine such as 27 → 28. The fact that the photolysis of 1 with 2-cyanopyridine does not yield any imidazolinone 2 also argue against the azetine mechanism.



the addition of methanol to nitrile ylides reported by Padwa.[8]

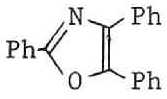
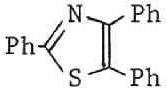
The result that benzil and 6 which has a α-cyanoethyl group were unable to be detected in the photolysis of 1 and AN in ethanol (Table 1,No 8) in sharp contrast to that in methanol (No 7) and the result that benzil and 6 were essentially not formed even in the presence of water in acetonitrile (No 3) are difficult to explain. However, it would be certain that they were formed by some ionic mechanisms. A tentative mechanism is shown in Scheme 1 which involves protonation of the long-lived ion pair 15, proton being provided by methanol. When methacrylonitrile was used instead of AN, benzil was produced even in ethanol (Table 2). This fact is puzzling, but may be understood, if we notice that the anion radical of methacrylonitrile will protonate more easily than that of AN, because a resultant radical 19 is more stable in the case of R=Me. In the case of photolysis of 12 in acetonitrile, decay of 15 to the ground state imidazole and AN is considered predominant over the route to lead to the corresponding imidazolinone.

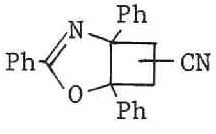


19 R=H or Me

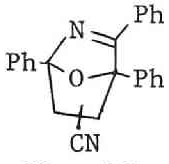
Similar irradiation of 2,4,5-triphenyloxazole (20) and 2,4,5-triphenylthiazole (21) with AN afforded no corresponding oxazolinone and thiazolinone, but gave only cycloadducts (Table 4). This may be due to much less basic character of oxazoles and thiazoles than imidazoles[9], and consequently due to higher ionization potential of the former two azoles which would become as a result more difficult to yield an ion pair such as 15.

Table 4. Photochemical reaction of 2,4,5-triphenyloxazole and 2,4,5-triphenylthiazole with AN.

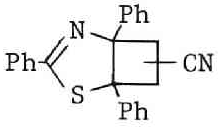
Azoles (Az)	Mx10^2	Mole ratio of AN/Az	Solv.	Irradn. time (hr)	Products(%)				Recovered Az(%)
					22a	22b	23a	23b	
 20	2.76	110	MeCN	9	20	26	5	17	13
					24a	24b	25	26	
 21	2.95	130	MeCN	15.5	21	14	8	8	45
	2.76	140	EtOH	17	24				72
	2.91	120	C_6H_6	17	9	5	3	3	76



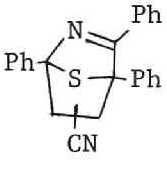
22a, 22b



23a, 23b



24a, 24b



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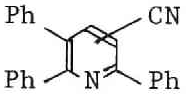


26

Scheme 3.

A comparison of the UV spectra of 22a, 22b, 23a and 23b with those of cis-2,4,5-triphenyloxazoline and N-benzylidenebenzylamine indicated that the former two were [2 + 2] adducts and the latter two [2 + 4] adducts. This assignment was supported by the facts that the infrared absorption attributable to C=N double bond appeared at a higher frequency with 22a and 22b than with 23a and 23b and that 23b easily underwent thermal cycloreversion to 20. (See Experimental.) The assignment that 24a and 24b are [2 + 2] adducts and 25 is a [2 + 4] adduct was assumed from the fact the irradiation of 24a and 24b did not yield 26, while 25 gave in a good yield 26 upon photolysis.[10] Upon photolysis 24a and 24b were interconverted (Scheme 3).

3. Experimental

All melting points are uncorrected. NMR, IR, UV and mass spectra were measured on a Varian T-60 spectrometer, a JASCO IRA-1 spectrometer, a Shimadzu UV-200 spectrometer and a HITACHI RMU-6C spectrometer, respectively. Column chromatography and thin layer chromatography (TLC) were carried out with Mallinckrodt silicic acid (100 mesh) and Merck Kieselgel GF_{254}, respectively. Preparative irradiation equipments and conditions are the same as those described in the preceding chapter. External irradiations (S and N ; see below) were carried out using a 400-W high pressure mercury lamp. Sample solutions were placed in Pyrex tubes of 20 ml volume. In the case of N, nitrogen was passed through the solution during irradiation to mix the solution. In the case of S, the solution was purged with nitrogen, sealed with a glass-stopper, and then irradiated.

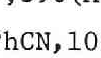
Materials.

All solvents and acrylonitrile(AN) were distilled before use. Commercial methacrylonitrile, crotononitrile, benzonitrile and 2-cyano-

pyridine were used as received. 1-Methyl-2,4,5-triphenylimidazole(1)[2]. 1,2,4,5-Tetraphenylimidazole(8)[12], 1,2-dimethyl-4,5-diphenylimidazole (12)[13], 2,4,5-triphenyloxazole(20)[12] and 2,4,5-triphenylthiazole(21)[14] were prepared by literature methods.

Photochemical Reaction of Imidazoles with AN (Table 1).

(A) 1-Methyl-2,4,5-triphenylimidazole(1). The photoreaction[-s] in acetonitrile and ethanol were described in the preceding chapter.

(a) In methanol. A solution containing 2.77 g of 1 in methanol (250 ml) and AN(110 ml) was irradiated with a 450-W lamp for 15 hr. The resultant AN polymer was filtered off and the distillation of the filtrate was carried out under reduced pressure to remove methanol and AN and then to afford 8 g of 3-methoxypropionitrile(7a)(bp ca.55°/12 mmHg; lit[15] 164-165°). The IR spectrum was idetical with an authentic one[15]. From the residue (4.76 g oil), recovered 1 crystallized out on standing overnight. After separating the crystals (700 mg), the residue was chromatographed on 100 g of silica gel. Elution with 800 ml of benzene, followed by preparative TLC (5:1 chloroform-benzene), afforded 110 mg of benzil (IR,NMR,TLC) and subsequently 50 mg (1.5%) of a Δ^3-imidazoline 6. In another similar run, 6 was obtained in a 4 % yield (Table 1). The structure of 6 was tentatively assigned on the basis of spectral data.[16] 6: colorless crystals,mp 194-197°(from ether); ν_{max}^{nujol} 2240(C≡N),1620, 1615,1295,1230,770,750,705,695 and 685 cm^{-1}; $\tau(CDCl_3)$ 2.03-2.88(17H,m,arom and $\underset{\underset{C}{\diagup}}{CH}=\underset{\diagdown}{CH}$ or $=CH_2$[16]),6.23(1H,quar,J=7Hz,CH_3-CH),7.78(3H,s,NCH_3) and 8.52 (3H,d,J=7Hz,CH_3-CH); λ_{max}^{EtOH} 253(ε15000) and 285(sh,3300)[16];m/e 416 (M^+,relative intensity <0.1),390($M^+-C_2H_2$,0.1),361(0.2),336(Ph-  ,91) 310(M^+-2AN,37) and 233(336-PhCN,100).(Found: C,80.80; H,5.78; N,13.53%. Calcd for $C_{28}H_{24}N_4$: C,80.74; H,5.81; N,13.45%). Further elution with 2.8 l of benzene gave a imidazolinone 2 (80 mg, IR,NMR,TLC), additional recovered 1(1.1 g) and additional 3-methoxypropionitrile(ca. 1 g). Further elution with 1.3 l of chloroform and then 200 ml of acetone, followed by preparative TLC of the eluate, yielded 180 mg of cycloadducts 3a and 3b (IR,NMR,TLC). Hydrolysis of 6 was carried out under the conditions similar to that of 2-[2-(2-phenyl-2H-imidazolyl)]propionitrile.[2] Thus, a solution of 6 (24 mg) in ethanol (3 ml) was heated at reflux

with 0.8 ml of dilute HCl(6%) on a water bath for 4 hr. After adding water(10 ml) the mixture was extracted with ether (20 ml x 2). The ethereal extract was dried over Na_2SO_4, and then evaporated. The residue was analyzed by VPC (silicone DC 550, 2 kg/cm^2 gauge, 200°) to show 71% yield of 2-benzoylpropionitrile[2](IR,VPC) and 33% yield of benzil(IR,VPC).

(b) External irradiation in various solvents. (i) In the presence of AN. After removing the AN polymer from the photolysates by filtration, residues were separated by preparative TLC (50:1 chloroform-acetone or 5:1 chloroform-benzene), and the products were characterized by NMR, IR and TLC. Yields in Table 1 are the isolation yields. (ii) In the absence of AN. Photolysates were analyzed by NMR, IR and TLC. Yields were determined by NMR (2-methylimidazole as the internal standard).

(B) 1,2,4,5-Tetraphenylimidazole(8).

(a) In acetonitrile. The photolysate (400-W lamp, 3 hr) from 970 mg of 8 in acetonitrile (300 ml) and AN (50 ml) was filtered to remove the AN polymer, evaporated under reduced pressure, taken up in hot chloroform (250 ml), filtered again, and finally evaporated again under reduced pressure. The residue was chromatographed on 70 g of silica gel. Elution with 400 ml of 1:1 benzene-chloroform, followed by preparative TLC (5:1 chloroform-benzene), afforded 60 mg of 1,2,4,4-tetraphenyl-Δ^2-imidazolin-5-one(9), 90 mg of a phenanthrene derivative 11, and subsequently 210 mg of recovered 8. The IR, NMR and mass spectra of 9 (mp 164.5-165.5°, lit[21] 157-158°) and the IR and NMR spectra of 11 (mp 211-212°, lit[3] 198-201°) were identical with those of authentic samples.[21,3] Further elution with the same solvent (400 ml) yielded additional 8 (210 mg) and 1,2-dicyanocyclobutanes(5)[2](250 mg, mainly cis-isomer judging from NMR). Further elution with the same solvent (400 ml) gave additional 5 (250 mg, mainly trans-isomer by NMR)

(b) In ethanol. The photolysate (400-W lamp, 6 hr) from 1.02 g of 8 in ethanol (300 ml) and AN (100 ml) was filtered, evaporated under reduced pressure, and chromatographed on 50 g Of silica gel. Elution with 1.3 l of ca. 2:1 benzene-chloroform afforded 510 mg of recovered 8.

Further elution with the same solvent (600 ml) followed by preparative TLC (50:1 chloroform-acetone) yielded in addition to a small amount of 5 and additional 8 (30 mg), cycloadducts 10a and 10b: 10a (more polar), 150 mg and 10b, 60 mg. 10a : colorless crystals, mp 214-216° (from benzene-ligroin), ν_{max}(nujol) 2240(C≡N),1595,1570,1500,775,720 and 690 cm^{-1}; τ($CDCl_3$) 2.16-3.44(20H,m,arom) and 6.03-7.29(3H,m,CH_2-CH); λ_{max} (Dioxane) 273(sh,ε5600),281(sh,4900)and 298(sh,4200)nm, no maximum above 273nm[22]; m/e 425(M^+,relative intensity 2) and 372(M^+-C_3H_3N,100). (Found : C,84.43; H,5.26; N,9.84 %. Calcd for $C_{30}H_{23}N_3$: C,84.67; H,5.45; N,9.88 %). The isolation of pure 10b was unsuccessful, but it must have a structure similar to 10a considering the NMR and IR spectra similar to those of 10a. 10b:ν_{max}(nujol) 2240(C≡N),1600,1570,1500,780,770 and 695 cm^{-1}; τ($CDCl_3$) 2.26-3.56(20H,m,arom) and 6.02-7.09(3H,m,CH_2-CH).

(C) 1,2-Dimethyl-4,5-diphenylimidazole(12).

(a) In acetonitrile. The photolysate (400-W lamp, 7 hr) from 1.01 g of 12 in acetonitrile (300 ml) and AN (50 ml) was worked up as described in (B)-(a). The residue was chromatographed on 70 g of silica gel. Elution with 700 ml of chloroform afforded 770 mg of 5. Further elution with chloroform (200 ml) yielded 350 mg of recovered 12. Further elution with chloroform (900 ml), followed by preparative TLC (5:1 chloroform-acetone), gave additional 12 (70 mg) and 130 mg of 1,2-dimethyl-1H-phenanthro[9,10-d]imidazole(14). 14 : colorless crystals, mp 197-201° (from acetone-petroleum ether);ν_{max}(nujol) 1540,770,765 and 720 cm^{-1}; τ($CDCl_3$) 1.23-1.60(3H,m,arom), 1.97-2.80(5H,m,arom), 6.39(3H, s,NCH_3) and 7.63(3H,s,CCH_3);λ_{max}(EtOH) 257(ε62000),282(10900),306(8500), 340(1300) and 356(1600) nm. (Found: C,82.63; H,6.00; N,11.13 %. Calcd for $C_{17}H_{14}N_2$: C,82.90; H,5.73; N,11.37 %). Further elution with 500 ml of 20:1 chloroform-acetone afforded additional 12 (70 mg).

(b) In ethanol. The photolysate (400-W lamp, 9.5 hr) from 1.00 g of 12 in ethanol (300 ml) and AN (50 ml) was filtered, and evaporated under reduced pressure. During the evaporation, some amounts of 3-ethoxypropionitrile(7b) was distilled out. The IR spectrum of 7b was identical with the authentic one.[15] The residue (1.80 g), which

contained ca.800 mg (NMR) of 7b, was chromatographed on 50 g of silica gel. After elution with 1 l of ca. 2:1 benzene-chloroform, 360 mg of recovered 12 was eluted with 900 ml of chloroform. Further elution with chloroform (200 ml), then with 20:1 chloroform-acetone (500 ml), afforded 400 mg of a cycloadduct 13a. Further elution with acetone (500 ml) followed by preparative TLC (5:1 chloroform-acetone) yielded additional 13a (70 mg) and 40 mg of 13b. Obviously, 13a and 13b have a similar structure judging from their NMR, IR and UV spectra.

13a : colorless crystals,mp 157-159°(from benzene-ether);ν_{max}(nujol) 2240(C≡N),1605,1600,1580,770 and 690 cm^{-1};τ($CDCl_3$) 2.63-3.20(10H,m, arom),6.09-7.33(3H,m,$C\underline{H}_2$-$C\underline{H}$), 7.44(3H,s,NCH_3) and 7.78(3H,s,CCH_3); λ_{max}(EtOH) 222(sh,ε20600) and 255(sh,4000)nm; m/e 301(M^+,0.9),300(1.4), 248(M^+-C_3H_3N,51) and 165(100). (Found : C,79.40; H,6.60; N,14.12 %. Calcd for $C_{20}H_{19}N_3$: C,79.70; H,6.35; N,13.94 %). It was unsuccessful to obtain analytically pure 13b : ν_{max}(nujol) 2240(C≡N),1600,1580,770, 710 and 695 cm^{-1};τ($CDCl_3$) 2.47-3.26(10H,m,arom), 6.24-7.00(3H,m,$C\underline{H}_2$-$C\underline{H}$), 7.46(3H,s,CH_3N) and 7.87(3H,s,CH_3C);λ_{max}(EtOH) 220(sh,ε16000) and 257 (3900)nm.

Oxygen-18 Incorporation Experiment with 1.

A Pyrex tube containing a solution of 125 mg of 1 and 40 μl of $H_2{}^{18}O$ (Prochem, 42.0 atm %) in acetonitrile (15 ml,distilled from P_2O_5 twice and then K_2CO_3) and AN (5 ml,distilled from K_2CO_3 twice) was sealed after bubbling nitrogen and irradiated externally with a 400-W high pressure mercury lamp for 13 hr. The photolysate was treated with the same procedures as described in (B)-(a) in order to remove the AN polymer. The residue was separated with preparative TLC (5:1 chloroform-benzene) to afford 48 mg (38 %) of recovered 1 and 12 mg (9 %) of ^{18}O-enriched 2. Then the latter was recrystallized from petroleum ether-chloroform to afford colorless crystals (mp 171.5-173°, lit[13] 165°) which was assayed mass-spectroscopically (M^+,M^++2) to contain 38.3 % ^{18}O in the carbonyl oxygen. Simultaneously, the mass spectra of authentic 2 and of 2 which was similarly treated with $H_2{}^{18}O$ were measured. Even a slight evidence for the presence of ^{18}O could

not be found in the latter spectra.

Photochemical Reaction of 1 with Various Nitriles (Table 2).

(A) With methacrylonitrile.

(a) In acetonitrile. The photolysate (450-W lamp, 9 hr) from 1.02 g of 1 in acetonitrile (250 ml) and methacrylonitrile (50 ml) was evaporated under reduced pressure, and the residue was chromatographed on 80 g of silica gel. After elution with 800 ml of benzene-chloroform(1:1), elution with 400 ml of benzene-chloroform(1:3) and then 400 ml of benzene-chloroform(1:5), followed by preparative TLC (50:1 chloroform-acetone), afforded 60 mg of 2 (NMR,IR,TLC), 55 mg of recovered 1 and 410 mg of 4 (NMR,IR). Further elution with 200 ml of benzene-chloroform(1:5) and 200 ml of chloroform, followed by preparative TLC (5:1 benzene-ethyl acetate or 25:1 chloroform-acetone), gave additional 1 (20 mg) and 4 (320 mg) in addition to large amounts (1.10 g) of methacrylonitrile polymers (NMR).

(b) In ethanol. The photolysate (450-W lamp, 9 hr) from 1.01 g of 1 in ethanol (250 ml) and methacrylonitrile (50 ml) was filtered and evaporated under reduced pressure. The residue (4.21 g) was chromatographed on 80 g of silica gel. Elution with 600 ml of benzene-chloroform (1:5), followed by preparative TLC (chloroform) and VPC (Silicone DC 550, 2 kg/cm^2 gauge, 200°), yielded 120 mg of benzil (NMR,IR,TLC). Further elution with the same solvent (300 ml) and then chloroform (400 ml), followed by preparative TLC (chloroform), afforded mixtures (770 mg) containing 1, 2, 4 and methacrylonitrile polymers (NMR,IR,TLC), but their isolation was unsuccessful due to large amounts of methacrylonitrile polymers.

(B) External irradiation with crotononitrile and benzonitrile.

The photolysates were analyzed by NMR, IR and TLC. Yields were determined by NMR (2-methylimidazole as the internal standard). Only in the crotononitrile case, preparative TLC (5:1 chloroform-benzene) was performed to isolate products.

Analytically pure 1-methyl-2-phenyl-1H-phenanthro[9,10-d]imidazole (4) was isolated in the preparative scale experiments with benzonitrile. Thus, the photolysate (400-W lamp, 24 hr) from 1.02 g of 1 and 18 ml of benzonitrile in ethanol (190 ml) was evaporated under reduced pressure

to give a viscous oil (1.73 g). On standing crystallized a part of the residue, which was separated by filtration (120 mg), and recrystallized from acetone to give 4: colorless crystals, mp 188-190°; ν_{max}(nujol) 750, 720, 710 and 695 cm^{-1}; $\tau(CDCl_3)$ 1.08-1.88(4H,m,arom), 2.12-2.67(9H,m,arom), 5.88(3H,s,CH_3); λ_{max}(EtOH) 258(ε64200), 285(18000), 305(sh,16700), 340 (5100) and 356(5100)nm. (Found: C,85.84; H,5.12; N,9.14 %. Calcd for $C_{22}H_{16}N_2$: C,85.69; H,5.23; N,9.09 %).

(C) With 2-cyanopyridine.

See the next chapter.

Photoaddition of AN to Oxazole 20 and Thiazole 21 .

(A) 2,4,5-Triphenyloxazole (20).

The photolysate (450-W lamp, 9 hr) from 2.05 g of oxazole 20 in acetonitrile (200 ml) and AN (50 ml) was filtered, evaporated, mixed with hot chloroform (200 ml), filtered again, and finally evaporated. The residue was chromatographed on 60 g of silica gel. Elution with chloroform (150 ml) recovered 85 mg of 20. Further elution with chloroform (300 ml), followed by preparative TLC (chloroform and/or 10-15 :1 petroleum ether-ethyl acetate), afforded in addition to additional 20 (185 mg) a series of cycloadducts 23a (130 mg), 23b (400 mg), 22a (490 mg) and 22b (320 mg) in the order of decreasing R_f value (chloroform as solvent). Further elution with chloroform (350 ml) gave additional 22b (310 mg). It was unsuccessful to secure analytically pure 23a. It is evident from the extraordinary similarity of IR and UV spectra that the structures of 22a and 22b are similar and so are those of 23a and 23b. Their physical data are as follows. 22a: colorless crystals, mp 123-125°(from ligroin); ν_{max}(nujol) 2235(C≡N), 1630,[24] 1330, 1300, 1275, 1050, 770, 760, 700 and 690 cm^{-1} ; $\tau(CDCl_3)$ 1.80-2.94(15H,m,arom) and 6.09-6.86(3H,m,CH_2-CH) ; λ_{max}(EtOH) 224(ε15700), 244(13500)and 286 (sh,1300)[25]nm. (Found : C,82.51; H,5.30; N,7.77 %. Calcd for $C_{24}H_{18}N_2O$: C,82.26; H,5.18; N,8.00 %). 22b : colorless crystals, mp 110-134° (from petroleum ether-acetone); ν_{max}(nujol) 2235(C≡N), 1630,[24] 1330, 1290, 1080, 1055, 1025, 770, 730, 690 and 670 cm^{-1}; $\tau(CDCl_3)$ 1.73-3.02(15H,m,arom) and 5.77-7.22(3H,m,CH_2-CH); λ_{max}(EtOH) 224(sh,ε15900), 245(12100) and 285(sh,800)[25]nm. (Found : C,82.62; H,5.65; N,8.03 %. Calcd for

$C_{24}H_{18}N_2O$: C,82.26;H,5.18; N,8.00 %). 23a : a colorless solid, mp 86-116° (reprecipitated from benzene-ligroin); ν_{max}(nujol) 2235(C≡N), 1590[24],1560,1315, 1010,770,740,700,690 and 675 cm^{-1} ; $\tau(CDCl_3)$ 1.92-2.95(15H,m,arom) and 6.57-7.86(3H,m,$C\underline{H}_2$-$C\underline{H}$); λ_{max}(EtOH) 250(ε12700)[25]nm. 23b : colorless crystals, mp 124.5-126.5°(from ether); ν_{max}(nujol) 2240(C≡N),1585,[24] 1560,1310,1025,760,735,710 and 685 cm^{-1}; $\tau(CDCl_3)$ 1.98-2.80(15H,m,arom) and 6.76-7.65(3H,m,$C\underline{H}_2$-$C\underline{H}$); λ_{max}(Dioxane) 250(ε 21800) and 283(sh,3400)[25]nm. (Found : C,81.97; H,5.21; N,7.78 %. Calcd for $C_{24}H_{18}N_2O$: C,82.26; H,5.18; N,8.00 %). On heating (ca 60°) 23b readily regenerated 20 (TLC,UV), supporting that it is a [2 + 4] adduct.

(B) 2,4,5-Triphenylthiazole(21).

(a) In acetonitrile. The photolysate (450-W lamp, 15.5 hr) from 2.31 g of 21 in acetonitrile (200 ml) and AN (50 ml) was similarly treated. The residue was chromatographed on 100 g of silica gel. Elution with 300 ml of benzene recovered 640 mg of 21. Further elution with benzene (300 ml), followed by preparative TLC (5:1 chloroform-benzene), yielded additional 21 (400 mg) and 210 mg of a cyano-triphenylpyridine 26, which was recrystallized from chloroform-ether to afford colorless crystals, mp 193.5-195.5°; ν_{max}(nujol) 2225(C≡N),1425,780,770 and 695 cm^{-1}; $\tau(CDCl_3)$ 1.82-2.95(m). (A singlet signal at τ 1.96 superimposed on the multiplet signal is attributable to proton on pyridine nucleus.) ; λ_{max}(Dioxane) 269(ε24900) and 310(sh,14000)nm; m/e 332(M^+, relative intensity 68) and 331(100). (Found : C,86.43; H,4.67; N,8.48 %. Calcd for $C_{24}H_{16}N_2$: C,86.72; H,4.85; N,8.43 %). Further elution with benzene (500 ml), followed by preparative TLC (5:1 chloroform-benzene, 30:1 benzene-ethyl acetate), successively yielded 24a (580 mg), 25 (210 mg) and 24b (330 mg). Further elution with benzene (200 ml) afforded additional 24b (40 mg). Successive elution with benzene (400 ml), chloroform (600 ml) and acetone (300 ml), followed by preparative TLC (50:1 chloroform-acetone), afforded 40 mg of an unidentified yellow solid ;ν_{max}(film) 2240(C≡N),1605,1570,1500, 1230,1050,765 and 690 cm^{-1}; $\tau(CDCl_3)$ 2.01-3.06(15H,arom), 5.45-5.66 (1H,m) and about 6.7-7.5(ca.3H,m). Purification of 25 by chromatography

was unsuccessful. Analysis of the UV spectra and the results of photolysis of 24a, 24b and 25 indicate that 24a and 24b are [2 + 2] adducts and 25 is [2 + 4] adduct. Their physical data are as follows. 24a : colorless crystals, mp 153.5-156°(from petroleum ether-acetone); ν_{max} (nujol) 2235(C≡N),1605,1595,1575,1235,960,785,770,765,690 and 680 cm^{-1}; $\tau(CDCl_3)$ 1.87-3.19(15H,m,arom) and 5.93-6.90(3H,m,CH_2-CH); λ_{max}(EtOH) 250(ε24200) and 283(sh,3900)[27]nm. (Found : C,78.83; H,4.71; N,7.63 %. Calcd for $C_{24}H_{18}N_2S$: C,78.67; H,4.95; N,7.65 %). 24b : colorless crystals, mp 155.5-157.5°(from ligroin-ethanol); ν_{max}(nujol) 2235(C≡N), 1605,1580,1265,1230,970,765,700,690 and 680 cm^{-1}; $\tau(CDCl_3)$ 1.85-3.05 (15H,m,arom) and 5.77-7.03(3H,m,CH_2-CH); λ_{max}(EtOH) 249(ε23500) and 283(sh,3200)[27]nm. (Found : C,78.65; H,5.02; N,7.44 %. Calcd for $C_{24}H_{18}N_2S$: C,78.67; H,4.95; N,7.65 %). 25 (ca 10 % of 24a (NMR) contained) : ν_{max}(film) 2235(C≡N),1600,1565,1495,1010,755 and 685 cm^{-1}; $\tau(CDCl_3)$ 2.06-3.06(15H,m,arom) and 6.53-7.43(3H,m,CH_2-CH); λ_{max}(EtOH) 254(ε 14400) nm.

(b) In ethanol and in benzene. The photolysate (450-W lamp,17 hr) from 1.73 g of 21 in ethanol (160 ml) and AN (40 ml) or from 1.73 g of 21 in benzene (155 ml) and AN (35 ml) was filtered and evaporated. A part of the residue was separated by preparative TLC (chloroform) in order to determine the yields.

Photolysis of 24 and 25.

Three sample solutions containing 24a (40 mg), 24b (37 mg) and 25 (9 mg), respectively, in acetonitrile (20 ml) were externally irradiated under the condition S (vide supra) for 18 hr(24a and 24b) or 11 hr (25). The photolysates from 24a and 24b were separated by preparative TLC (4:1 chloroform-benzene) to yield recovered 24a (14 mg, 35 %) and 24b (7 mg, 18 %) from the former and to yield 24a (6 mg, 16 %) and recovered 24b (17 mg, 46 %) from the latter. In addition, a pale yellow solid having the largest R_f value was isolated (15 mg from the former and 14 mg from the latter); ν_{max}(nujol) 1275,1075,1030,770,750,725,700 and 690 cm^{-1}. The photolysate from 25 was found to contain only 26 (TLC, IR).

Fluorescence Quenching and Quantum Yield Measurements.

Methods and conditions are the same as those described in the preceding chapter. Results of quantum yield experiments for the formation of 2, which was assayed by TLC (2.5:1 chloroform-benzene) using benzophenone as the internal standard, are shown in Table 5 and Figure 2.

Table 5. Quantum yields for the formation of 2 in acetonitrile.

[AN] M	0.0503	0.101	0.302	1.01
$\Phi \times 10^4$	3.5	4.8	6.2	7.4

[1] = 6.28×10^{-3} M

Results of the fluorescence quenching of 1 are shown in Figure 1. (Maximal wavelength of fluorescence ; 400 nm in acetonitrile and 397 nm in ethanol.)

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10. As a matter of fact, the photo-extrusion of a sulfur atom from type (A) compounds is known,[11] but the reaction from type (B) compounds appears unknown.

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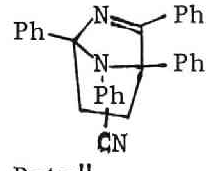
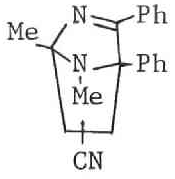
21. Private communication with Dr. I. Saito of our laboratory.

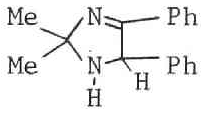
22. These data are inconsistent with the structure of [2 + 4] adduct shown below, considering the UV spectra of phenyl-substituted imines[2] and N,N-dimethylaniline [λ_{max}(EtOH) 251 (ε12500) and 297(1600) nm; J. P. Phillips and F. C. Nachod (Ed.), "Organic Electronic Spectral Data", Interscience Publ., New York, London, Vol. I (1957), p. 216].



23. These data are inconsistent with the structure of a [2 + 4] adduct 29, considering the UV spectra of 30; λ_{max}(95 % EtOH) 245 (ε 12500) nm.[2]



29



30

24. These are attributed to the C=N double bond absorption. As seen in the following example ; PhC(Me)=N-Ph 1630 (solid) cm^{-1}, Ph-C(OMe)=N-Ph 1666 cm^{-1} [J. Fabian and M. Legrand, Bull. Soc. Chim. France, 1461 (1956)], imino ethers have higher frequencies than imines. This is consistent with the assignment that 22a and 22b are [2 + 2] adducts and 23a and 23b are [2 + 4] adducts.

25. The spectra of 22a and 22b are similar to that of cis-2,4,5-triphenyloxazoline[26] [222(sh, ε15000), 242(13400) and 286(sh, 900) nm]. On the other hand, the spectra of 23a and 23b, which are similar to that of $PhCH_2$-N=CH-Ph [λ_{max}(EtOH) 250 (ε20800) and 280 (sh, 2080)[2] nm], are different from that of this oxazoline.

26. M. Svoboda, J. Sicher, J. Farkaš and M. Panková, Collection Czechoslov. Chem. Commun., 20, 1426 (1955).

27. cf. 2-Phenylthiazoline[28] : λ_{max}(EtOH) 241(ε14900) and 271(sh, 3000) nm.

28. H. Wenker, J. Amer. Chem. Soc., 57, 1079 (1935).

C H A P T E R III

The Photochemical Reaction between Imidazoles and 2-Cyanopyridine

Upon photolysis, 1-methyl-2,4,5-triarylimidazoles 1 and 7 react with 2-cyanopyridine(2), probably via exciplexes, to afford 1:1 adducts 3 and 8, respectively, in addition to a bipyridine-carbonitrile 4 and other products. The structure of the adducts 3 and 8 was assigned as a [2 + 2] cycloadduct between the C_4=C_5 double bond of the imidazoles and the cyano group of 2 on the basis of spectral and chemical evidences. The adducts were found to undergo a novel reaction by treatment with methanol-hydrochloric acid to give a Δ^2-imidazoline 10 or 11 (Scheme 1). A mechanism for the formation of 3, 8 and 4 involving chemically sensitizing action of imidazoles is presented. (Scheme 2)

1. Introduction

Photochemical cycloadditions of π-systems to a cyano group are rare. Recently Cantrell[1a] and Blackwell, et al.[1b] have reported [2 + 2] photocycloaddition of the cyano group with olefines and thiones as an intermediate step to final products.[2]

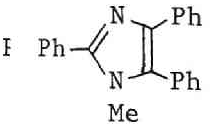
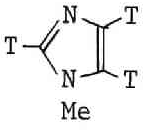
In this chapter the author wishes to present the photochemical cycloaddition of 2-cyanopyridine with imidazoles and the imidazole-sensitized condensation of 2-cyanopyridine. The former reaction is probably the first example that photocycloadducts between C=C and C≡N bonds were isolated.

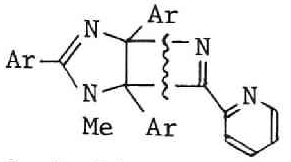
2. Results and Discussion

Irradiation of 1 or 7 with an excess of 2-cyanopyridine(2) where 1 or 7 absorbs most of the light, yielded a 1:1 adduct 3 or 8 and a bipyridine-carbonitrile 4 and a terpyridine-carbonitrile 5 (Table 1). The quantum yield for the formation of 3 was 6.0×10^{-4} for a solution of 6.45×10^{-3} M of 1 and 4.10×10^{-2} M of 2 in acetonitrile and was about twice that of the photochemical formation of 2,4,4-triphenyl-Δ^2-imidazolin-5-one from 1 and acrylonitrile.[3]

The structure of 3 was assigned on the basis of the spectral data. Although the structure 3' is consistent with the mass fragmentation and the reaction with dilute hydrochloric acid in methanol (vide infra), its posibility was eliminated, because the lack of infrared absorption in the region of C≡N clearly demonstrates the participation

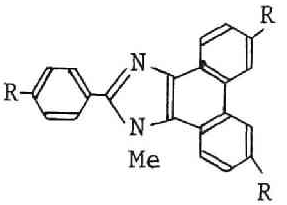
Table 1. Photochemical reaction of imidazoles 1 and 7 with 2-cyanopyridine(2).

Imidazole(Im) M x 10^2	Mole ratio of 2/Im	Solv.	Irradn. time (hr)	Products (%)[a]				Recovered (%)	
				3	4	5	6	Im	2
 0.996	4.2	MeCN	13	48	40	4	19	4	37
1.33	4.4	MeCN	27	52	35	—	3	0	33
1.34	4.3	EtOH	27	7	3	—	11	69	88
1									
				8	4	5	9		
 1.17	5.5	MeCN	12	42	36	3	24	5	45
7									



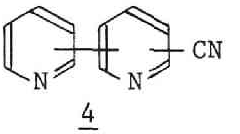
3; Ar=Ph

8; Ar=p-tolyl(T)

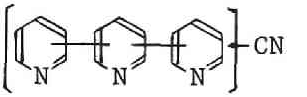


6; R=H

9; R=Me



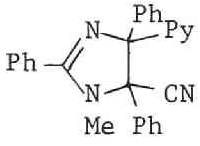
4



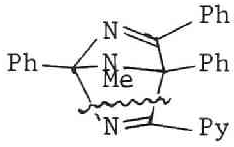
5

a) Yields are based on the initial amount of the imidazoles except 4 and 5, where they were calculated based on the initial amount of 2.

of the cyano group in the adduct formation. Furthermore, the NMR spectrum of the adduct shows that pyridine nucleus is intact in this photoreaction. At this stage, an unambiguous decision could not be made as to whether the adduct has a [2 + 2] (3) or [2 + 4] (3") cyclo-adduct structure. However, the former structure appeared preferable



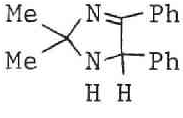
3'

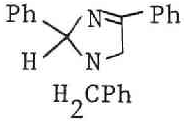


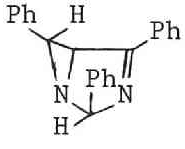
3"

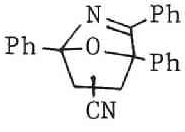
(Py = α-pyridyl)

from the UV spectra of the phenyl-substituted imines, $PhC(R)=NR'$ [3,4]. As seen below, the ultraviolet absorption of imines usually appears in





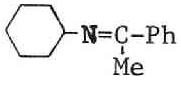


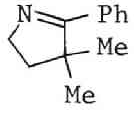


$PhCH_2$-N=CHPh

Solvent	95%EtOH	MeOH	95%EtOH	Dioxane	EtOH
λ_{max} nm	245	247	245	250	250
(ε)	(12500)	(12400)	(20000)	(21800)	(20800)
				283	280
				(sh,3400)	(sh,2080)

n-Bu-N=CHPh

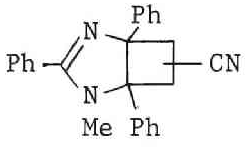




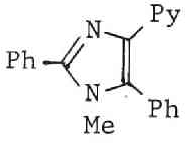
Solvent	EtOH	EtOH	EtOH
λ_{max} nm	246 (14500)	240	239
(ε)	280 (1520)	(10000)	(8900)
	288 (1000)		

240 - 250 nm region with a large molar extinction coefficient ($\varepsilon > 10^4$). The spectrum of 3 [λ_{max}(EtOH) 220(sh,ε 24600), 260(7800) and 272(sh, 6000) nm with minimum absorption at 246(ε 6000) nm], however, has no

maximum in 240 - 250 nm region. This may eliminate the [2 + 4] structure (3''). The UV spectrum of 3 is approximately equal to the sum of the spectra of 7-cyano-4-methyl-1,3,5-triphenyl-2,4-diazabicyclo[3,2,0]-hept-2-ene (13)[4] and 2-cyanopyridine.



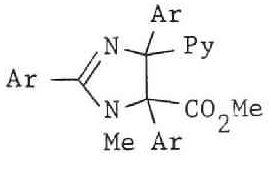
13



14 (Py = α-pyridyl)

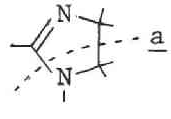
The azetine structure for the 1 : 1 adduct (3) was also supported by the result of pyrolysis of 3 leading to the original imidazole 1 in 57 % yield. If the adduct had the [2 + 4] structure (3''), an imidazole 14 would be formed along with 1 through indiscriminate losses of 2-cyanopyridine and benzonitrile from 3''. However, the imidazole 14 could not be detected among products. A similar result was obtained with pyrolysis of 8 (vide infra).

On hydrolysis with dilute hydrochloric acid in methanol, 3 was transformed into a Δ^2-imidazoline 10 (67 %) whose structure was assigned by its spectral data. Mass spectroscopy was a potent tool for the determination of the substitution pattern of 10, because base peaks of Δ^2-imidazolines 12 are in many cases generated by type a fragmentation[5]. In the mass spectrum of 10 [447(M^+, relative inten-



10; Ar = Ph

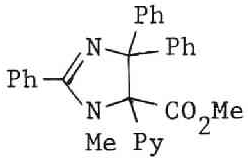
11; Ar = p-tolyl



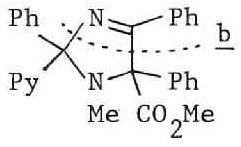
12

(Py = α-pyridyl)

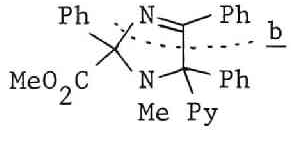
sity 0.1), 416(M^+-OCH_3, <0.05), 388($M^+-CO_2CH_3$, 2.5), 310($\underline{1}^{+\cdot}$, 2), 270(Ph-(N=C(Ph)-Py)$^{+\cdot}$, 100), 167(Ph-$\overset{\cdot}{C}$-Py, 45), 139(16) and 118(Ph-$\overset{+}{C}$=N-CH_3, 53)][6](Py = α-pyridyl), peaks at m/e 270, 167 and 118 cannot be explained by other Δ^2-imidazoline structures such as 10'. The UV



10'



10"



10'" 1

spectrum of 10 [λ_{max}(EtOH) 220(sh, ε17000) and 263(4800) nm] is approximately equal to the sum of the spectra of 13 [λ_{max}(EtOH) 222 (sh, ε18300) and 266(2500) nm or λ_{max}(EtOH) 222(sh, ε16800) and 266 (3000) nm][4] and 2-picoline [λ_{max}(EtOH) 256(ε2000), 262(2200) and 269 (1700)][8]. This agreement supports the structure of 10. Δ^3-Imidazolines such as 10" and 10'" cannot explain the UV spectrum of 10, considering the UV data of phenyl-substituted imines shown above. The mass spectrum of 10 is also inconsistent with the structure 10" and 10'". The Δ^3-imidazolines are expected to follow the type b fragmentation.[7]

The mass spectrum of 3 [414(M^+,0.5),310(1.5),270(100),167(62),139 (23) and 118(11)] is noteworthy, since it is very similar to that of 10 in the region below m/e310. The mass spectrum of 3 and the transformation of 3 into 10 can be interpreted by Scheme 1.# As a result, the relative orientation of the two addends in 3 is assigned as shown in Scheme 1.

The ambiguity due to the small difference in mass number between phenyl(=77) and pyridyl(=78), which may lead to erroneous interpretation of the mass spectra of 3 and 10, was eliminated by replacing phenyl groups with p-tolyl groups. Thus, analysis of the mass spectra of 8 and

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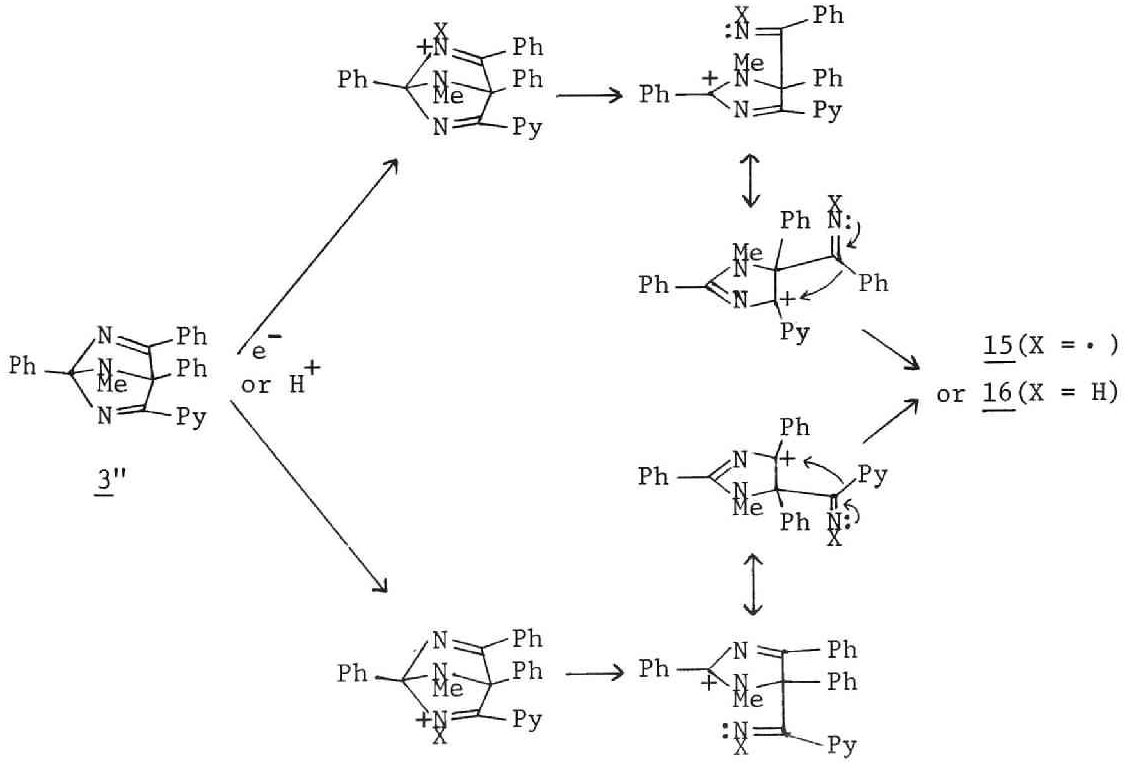
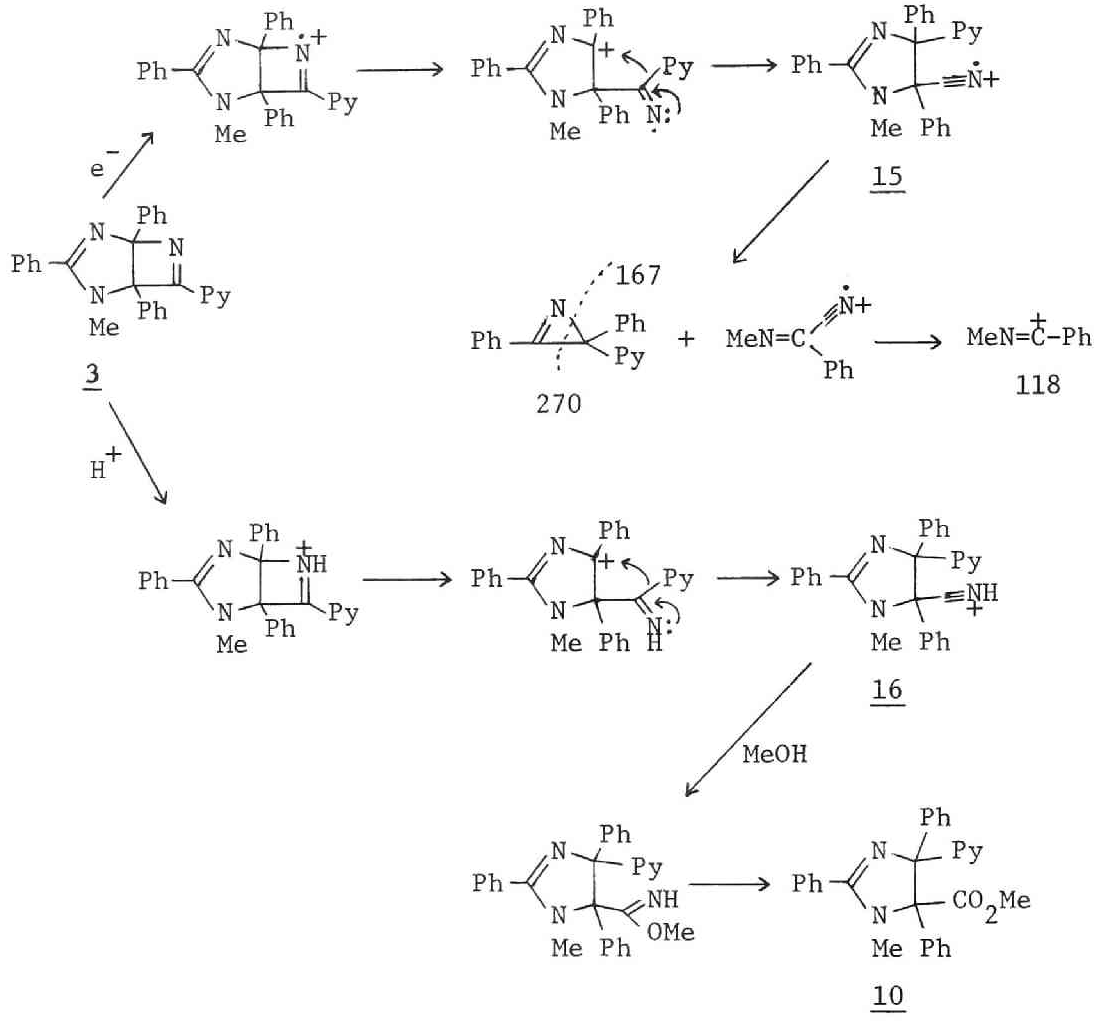
If the true structure of the 1:1 adduct is 3", pathways shown below can be considered. (Py=α-pyridyl, X=•in the case of the mass spectroscopic fragmentation or H in the case of the acid-hydrolysis)



Scheme 1

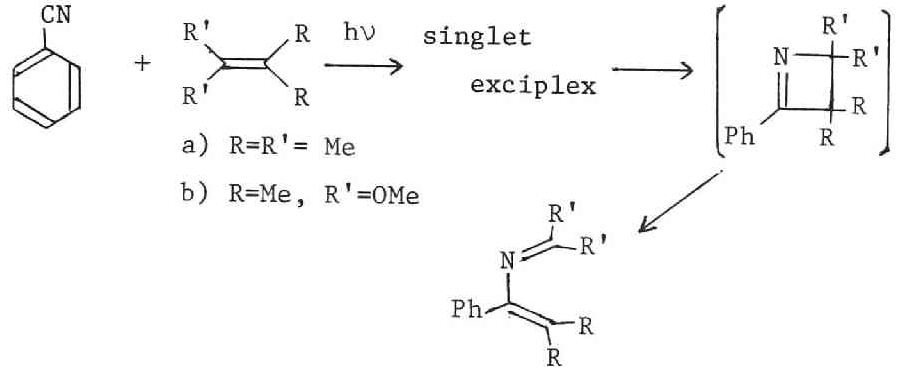


(Py = α-pyridyl)

11 (see section 3) supports the above interpretation. The preparation 8 and 11 was done in the same way as 3 and 10. Pyrolysis of 8 and 11 gave 7 in yields of 48 % and 2 %, respectively. To the light through Pyrex 8 was fairly stable.

The photochemical [2 + 2] cycloaddition of a cyano group with

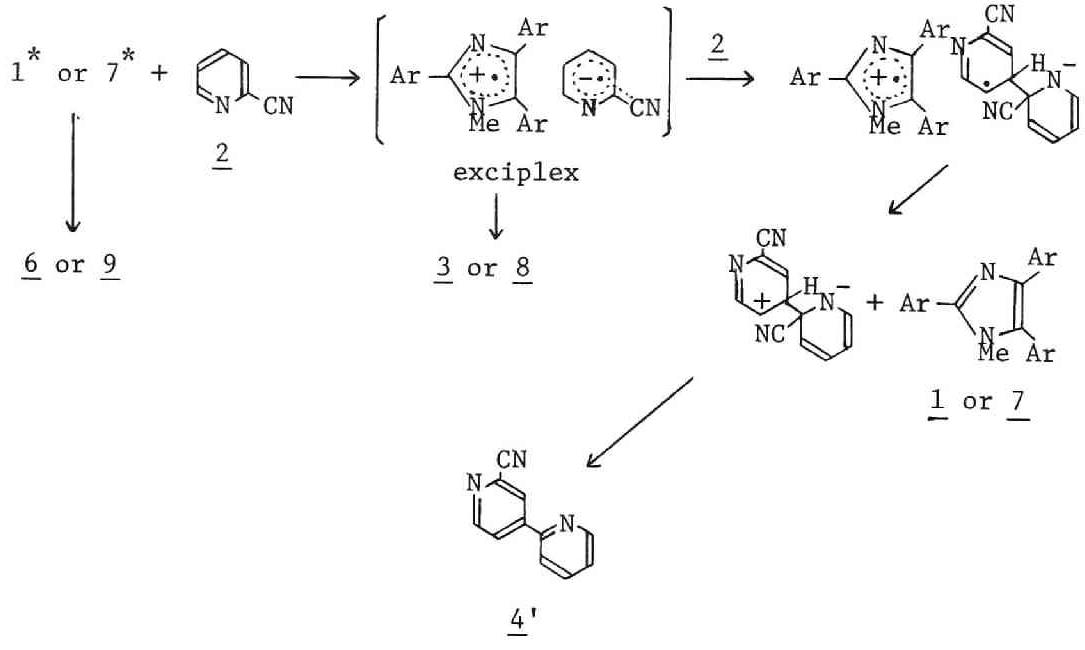
olefinic double bonds giving an azetine has been recently reported to occur as an intermediate step of the photoreaction between benzonitrile and electron rich olefins, and singlet exciplexes have been assumed to be involved.[1a] This reaction is illustrated below. Nevertheless, the present photoreaction found by the author seems to be the first example that [2 + 2] photocycloadducts were isolated.

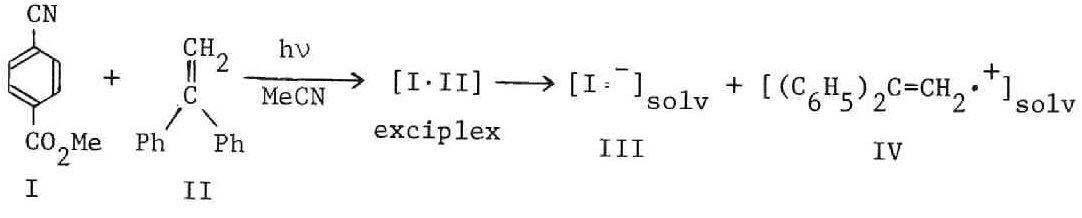


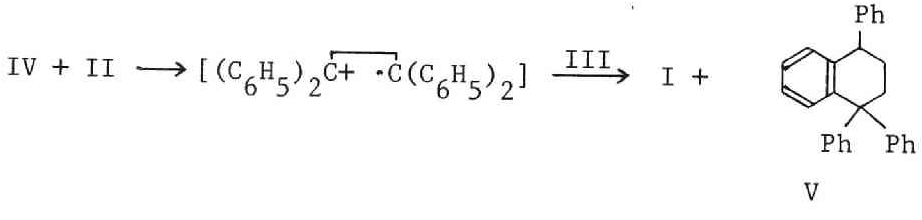
The mechanism for the formation of 4 and 5 is not yet clear. Irradiation of 2-cyanopyridine alone did not yield 4 and 5, even in the presence of triplet sensitizers such as benzophenone, xanthone and acetone. Therefore, the excited 2-cyanopyridine does not seem responsible for this reaction. It is also to be noted that the yield of 4 in acetonitrile did not increase by prolonged irradiation, where most of the imidazole 1 was consumed (Table 1). These facts mean that the excited imidazole plays an important role for the formation of 4. A tentative mechanism for the formation of 3 (or 8) and 4 is shown in Scheme 2. Fluorescence quenching of 1 by 2-cyanopyridine with linear Stern-Volmer plots (Figure 1) and a large enhancement of this reaction in acetonitrile relative to in ethanol (Table 1) support the presence of polar

exciplex intermediates. As depicted in Scheme 2, the action of imidazoles 1 and 7 like a chemical sensitizer or an electron transfer catalyst in the formation of 4 is most probable. This is supported by

Scheme 2







simple calculations that the molar quantity of 4 produced in acetonitrile was larger than the difference in molar quantity between the imidazole 1 (or 7) employed and the cycloadduct 3 (or 8) produced (Table 1). It should be noted that in the photochemical dimerization of 1,1-diphenylethylene (II) to a tetrahydronaphthalene derivative, V,[9] methyl p-cyanobenzoate (I) acts as an electron transfer catalyst in a similar manner to the imidazole--2-cyanopyridine case. The structure of 4 is most probably given by formula 4', because the anion radical of 2 may attack the 4-position having the largest positive charge density among the four unsubstituted positions of the 2-cyanopyridine nucleus.[10]

3. Experimental

All melting points are uncorrected. NMR, IR, UV and mass spectra were measured with the same instruments described in the preceding chapter.[3] Preparative irradiations were carried out with a 400-W or 450-W high pressure mercury lamp surrounded by a Pyrex cooling jacket under bubbling nitrogen. External irradiations were carried out using a 400-W high pressure mercury lamp in a Pyrex tube which had been closed after placing the sample and bubbling nitrogen before irradiation.

Photolysates were separated by column chromatography (Mallinckrodt silicic acid, 100 mesh) and/or thin layer chromatography (Kieselgel GF_{254}, Merck), after removing solvents under reduced pressure.

Materials.

Commercial 2-cyanopyridine was recrystallized from ether. 1-Methyl-2,4,5-triphenylimidazole(1).[4] 1-Methyl-2,4,5-tri(p-tolyl)-imidazole(7) was prepared by methylation of 2,4,5-tri(p-tolyl)imidazole[11]

according to the synthesis of 1.[4] 7: colorless crystals, mp 150-151.5° (from 10:1 methanol-water); ν_{max}(nujol) 1520,1495,825,820 and 735 cm^{-1}; $\tau(CDCl_3)$ 2.27-3.09(12H,m,arom),6.56(3H,s,CH_3N),7.58(6H,s,CH_3C) and 7.73(3H,s,CH_3C); λ_{max}(EtOH) 225(sh,ε24000) and 286(21100) nm. (Found : C,84.90; H,6.83; N,7.68%. Calcd for $C_{25}H_{24}N_2$: C,85.19; H,6.86; N,7.95%).

Photolysis of 1 and 2-cyanopyridine(2).

(a) In acetonitrile. The photoproduct mixture (400-W lamp, 13 hr) from 1 (1.08 g) and 2 (1.54 g) in acetonitrile (350 ml) was chromatographed on 80 g of silica gel. Elution with 600 ml of benzene, followed by preparative TLC (5:1 chloroform-benzene), afforded two unidentified materials A (13 mg, more polar) and B (14 mg), which seem isomeric, considering their NMR and IR spectra. Product A : yellow crystals, mp 149-154° (from ligroin); ν_{max}(film) 1615,1580,1500,1305, 1250,1230,1215,1065,1030,970,780,770,740 and 690 cm^{-1}; $\tau(CDCl_3)$ 2,17-2.84(15H,m,arom) and 7.53(3H,s,CH_3);λ_{max}(EtOH) 259(ε12700) nm; m/e 362 (relative intensity,0.2),361(0.8),335(0.7),310(1.3),285(8),259(83) and 218(100). (Found: C,79.99; H,4.95; N,15.09%. Calcd for $C_{24}H_{18}N_4$: C, 79.53; H,5.01; N,15.46%). Product B: resisted to crystallization; ν_{max}(film) 1615,1580,1500,1305,1250,1220,1065,1045,770,765,740 and 690 cm^{-1}; $\tau(CDCl_3)$ 2.10-2.80(15H,m,arom) and 7.70(3H,s,CH_3). They were not further studied. Further elution with 800 ml of benzene afforded 370 mg of a 1:1 cycloadduct(3): colorless crystals, mp 188-190°(from ether); ν_{max}(nujol) 1620,1590,1060,750 and 700 cm^{-1}; $\tau(CDCl_3)$ 1.20-1.39(1H,m, )[12], 2.00-3.15(18H,m,arom) and 7.27(3H,s,CH_3);UV and mass spectra, see section 2. (Found: C,81.33; H,5.34; N,13.43%. Calcd for $C_{28}H_{22}N_4$: C,81.13; H,5.35; N,13.52%). Further elution with 1.5 l of benzene, followed by preparative TLC(50:1 chloroform-acetone), yielded additional 3 (190 mg) and recovered 2 (550 mg). Further elution with 600 ml of chloroform followed by preparative TLC(50:1 chloroform-acetone) gave additional 3 (130 mg) and 2 (30 mg), 6 (200 mg, identified by NMR and IR), recovered 1 (40 mg), and 450 mg of a bipyridine-carbonitrile(4)[13]. 4: colorless crystals,mp 161.5-162°(from chloroform-ether);ν_{max}(nujol) 2240(C≡N),1590,1000 and 785 cm^{-1}; $\tau(CDCl_3)$1.09-1.30(2H,m, )[12],

1.53-2.72(5H,m);λ_{max}(EtOH) 219(ε21100),249(10200) and 278(14100);m/e 181(M^+,relative intensity 100),154(M^+-HCN,63) and 131(metastable peak). (Found: C,73.04; H,3.63; N,23.12%. Calcd for $C_{11}H_7N_3$: C,72.91; H,3.89; N,23.19%). Further elution with 1 l of chloroform followed by preparative TLC (50:1 chloroform-acetone) afforded additional 4 (90 mg) and 55 mg of a terpyridine-carbonitrile 5. 5: light brown crystals,mp 169-170.5° (from acetone-ether);ν_{max}(nujol) 2240(C≡N),1590,855 and 780 cm^{-1}; τ($CDCl_3$) 1.08-2.74(m);λ_{max}(EtOH) 225(ε24700),245(sh,21500) and 276 (18500);m/e 258(M^+,relative intensity 100) and 169(96). (Found:C,74.30; H,3.75; N,21.46%. Calcd for $C_{16}H_{10}N_4$: C,74.40; H,3.90; N,21.70%).

In the case of prolonged irradiation, the photolysate (450-W lamp, 27 hr) from 1.03 g of 1 and 1.52 g of 2 in acetonitrile (250 ml) was treated similarly (silica gel, 90 g). The result is shown in Table 1.

(b) In ethanol. The photolysate (450-W lamp, 27 hr) from 1 (1.04 g) and 2 (1.52 g) in ethanol (250 ml) was treated similarly (silica gel 90 g). The result is shown in Table 1.

Photolysis of 7 and 2-cyanopyridine(2).

The photoproduct mixture (400-W lamp, 12 hr) from 1.44 g of 7 and 2.35 g of 2 in acetonitrile (350 ml) was separated by silica gel column (90 g). Elution with benzene(2.3 l), followed by preparative TLC (50:1 benzene-acetone or 80:5:1 chloroform-petroleum ether-acetone), afforded 790 mg of 8, 1.06 g of recovered 2, 350 mg of 9 and 70 mg of recovered 7. Further elution with chloroform (1.1 l), followed by preparative TLC (50:1 chloroform-acetone), gave 4 (740 mg) and 5 (65 mg). 8 : colorless crystals,mp 200-201° (from ether-acetone);ν_{max}(nujol) 1620,1590,1525, 1065,830,825 and 755 cm^{-1}; τ($CDCl_3$) 1.23-1.38(1H,m, )[12], 1.98-3.36 (15H,m,arom),7.29(3H,s,CH_3N),7.57(3H,s,CH_3C),7.73(3H,s,CH_3C) and 7.85 (3H,s,CH_3C);λ_{max}(EtOH) 228(ε28200),259(9300),265(sh,9000) and 272(sh, 7200) nm; m/e 456(M^+,relative intensity 0.1),352(M^+-2,0.5),298(T-  $^{+\cdot}$ 100),180(T-$\overset{+\cdot}{C}$-Py-1,64),143(28) and 132(T-$\overset{+}{C}$=N-Me,26) (T=p-tolyl). (Found: C,81.26; H,5.98; N,12.05%. Calcd for $C_{31}H_{28}N_4$: C,81.54; H,6.18; N,12.27%). 9: colorless crystals, mp 263-264° (from acetone-chloroform); ν_{max}(nujol) 1540,1180,830,805 and 730 cm^{-1} ; τ($CDCl_3$) 1.26-1.87 and 2.26-2.80(10H,m,arom),5.85(3H,s,CH_3N),7.39(6H,s,CH_3C) and 7.57

(3H,s,CH_3C);λ_{max}(EtOH) 255(sh,ε46600),263(64500),292(17700),309(13800), 349(3900) and 366(4100)nm, (Found: C,85.68; H,6.21; N,7.84%. Calcd for $C_{25}H_{22}N_2$: C,85.68; H,6.33; N,7.99 %).

Hydrolysis of 3.

A solution containing 104 mg of 3 and 0.5 ml of 35 % hydrochloric acid in methanol (5 ml) and benzene(3 ml) was heated on a water bath (52-57°) for 5.5 hr. The reaction mixture was neutralized to pH 8 with 5 % aqueous NaOH, mixed with 20 ml of water, and extracted with 30 ml of ether twice. The extracts were dried over Na_2SO_4, evaporated under reduced pressure, and the residue was separated with preparative TLC (50:1 chloroform-acetone) to yield 29 mg of recovered 3 and 54 mg (67 %) of 5-carbomethoxy-1-methyl-2,4,5-triphenyl-4-(α-pyridyl)imidazoline(10), which recrystallized from ethanol-petroleum ether to afford colorless crystals; mp 209.5-211°;ν_{max}(nujol) 1735(CO_2Me),1625,1590, 1215,1195,1060,1025,785,760,750,705 and 690 cm^{-1};τ($CDCl_3$) 1.30-1.49 (1H,m, )[12], 2.13-3.24(18H,m,arom),6.54(3H,s,OCH_3) and 7.32(3H,s, NCH_3);λ_{max}(EtOH) and m/e, see section 2. (Found: C,77.57; H,5.39; N,9.25 %. Calcd for $C_{29}H_{25}N_3O_2$: C,77.83; H,5.63; N,9.39 %).

Hydrolysis of 8.

A solution containing 250 mg of 8 and 1 ml of 35 % hydrochloric acid in methanol(10 ml) and benzene(5 ml) was treated similarly (50:1 benzene-acetone as a preparative TLC solvent) to yield 30 mg of reverted 8 and 150 mg (64 %) of a imidazoline 11 which was recrystallized from ethanol-ligroin to afford colorless crystals, mp 202-205°; ν_{max}(nujol) 1740(CO_2Me),1630,1590,1215,1180,1065,1035,830 and 750 cm^{-1}; τ($CDCl_3$) 1.40-1.56(1H,m, )[12],2.30-3.47(15H,m,arom),6.58(3H,s,OCH_3), 7.34(3H,s,NCH_3),7.59(3H,s,CCH_3),7.83(3H,s,CCH_3) and 7.92(3H,s,CCH_3); λ_{max}(EtOH) 222(sh,ε21700) and 265(6100)nm; m/e 489(M^+, relative intensity 0.05),458(M^+-OMe,0.03),430(M^+-CO_2Me,6.5),352( ,1.1),298 (T-  ,100),180(T-$\overset{+}{C}$-Py-1,61) and 132(T-$\overset{+}{C}$=N-Me,85). (Found:C,78.28; H,6.45; N,8.34%. Calcd for $C_{32}H_{31}N_3O_2$: C,78.50; H,6.38; N,8.58%).

Pyrolysis of 3.

Under reduced pressure (35-45 mmHg) 144 mg of 3 was heated at 220-221° for 5 hr. The volatile products which were collected by a ice-water trap during the pyrolysis contained <0.5 mg of benzonitrile(VPC

analysis). The nonvolatile products were separated by preparative TLC (50:1 benzene-acetone) to afford 10 mg of recovered 3 and 57 mg(57 %) of 1. NMR and TLC analyses of the nonvolatile products before and after the separation with preparative TLC showed no evidence for the formation of an imidazole 14.

Pyrolysis of 8 and 11.

Under reduced pressure (25-30 mmHg) 160 mg of 8 was heated at 200 -204° for 4 hr and the reaction mixture was separated by preparative TLC (50:1 benzene-acetone) to afford 70 mg of recovered 8 and 33 mg (48 %) of 7 (NMR, IR).

Similar treatment of 35 mg of 11 at 190-200° for 2 hr yielded 4 mg of recovered 11 and 1 mg of 7 (TLC, IR, NMR).

Photolysis of 8.

A solution of 8 (138 mg) in acetonitrile (20 ml) was externally irradiated for 14 hr and the photolysate was separated by preparative TLC (60:1 benzene-acetone) to afford 123 mg of recovered 8 and 8 mg of an unidentified product (or products), which was obviously an isomer of 8 judging from the NMR and IR spectra : ν_{max}(film) 1620,1590,1520, 1065,830,820 and 760 cm^{-1}; $\tau(CDCl_3)$ 1.77-3.30(16H,m,arom),7.27(3H,s, CH_3N),7.55(3H,s,CH_3C),7.67(3H,s,CH_3C) and 7.76(3H,s,CH_3C).

Photolysis of 2-cyanopyridine (2).

2-Cyanopyridine (108 mg), a mixture of 2 (113 mg) and benzophenone (102 mg), and a mixture of 2 (107 mg) and xanthone (101 mg), respectively, dissolved in acetonitrile (20 ml) were externally irradiated for 24 hr and the photolysates were analyzed by NMR and TLC. Even a trace of 4 could not be detected in all cases, although a small amount of some products was observed in the sensitized cases.

2-Cyanopyridine (565 mg) in acetone (500 ml) was irradiated with a 400-W high pressure mercury lamp (Pyrex) under bubbling nitrogen for 18 hr and the photolysate was analyzed by TLC, preparative TLC, NMR and IR, but 4 could not be detected at all.

Fluorescence quenching and quantum yield measurements.

The apparatus and the conditions for measuring fluorescence intensities were the same as those described in the preceding chapter[4]

except irradiation wavelength (330 nm). The results are shown in Figure 1.

The quantum yield for the formation of 3 was measured on a merry-go-round apparatus using a 400-W high pressure mercury lamp (Pyrex) as the light source. To measure light intensity, the photoreaction of 1 with acrylonitrile in acetonitrile[3] was utilized. Yield of 3 was determined by TLC (30:1 benzene-acetone; benzophenone as the internal standard). For other details, see the previous chapter.[4]

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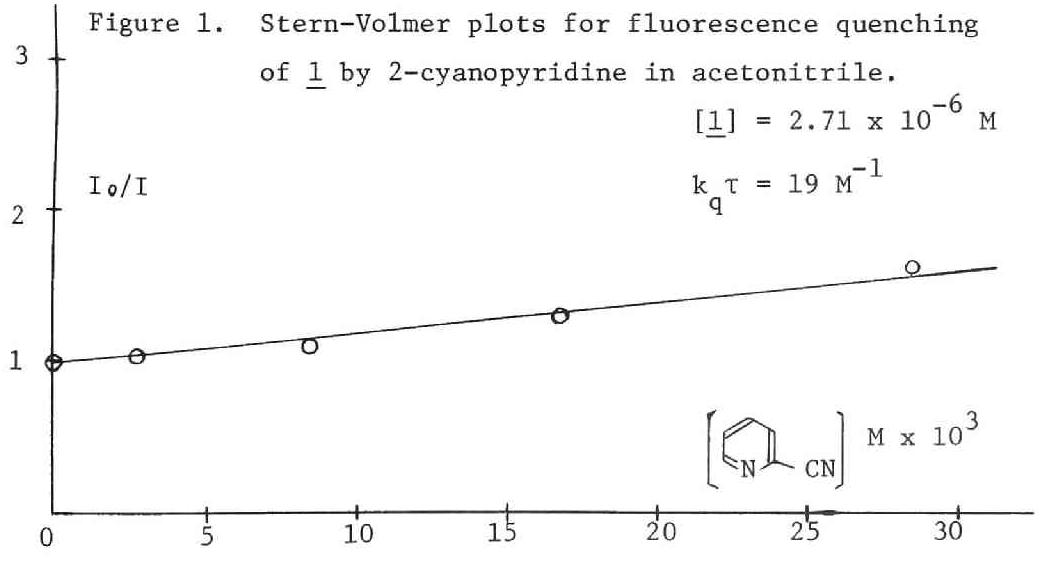
1. a) T. S. Cantrell, J. Amer. Chem. Soc., 94, 5929 (1972). b) D.S.L. Blackwell, P. de Mayo and R. Suau, Tetrahedron Letters, 91 (1973).
2. Photochemical [2+4] cycloaddition between π-systems and a cyano group appears to have no example.
3. Part II, Chapter II.
4. Part II, Chapter I
5. Q. N. Porter and J. Baldas,"Mass Spectrometry of Heterocyclic Compounds", John Wiley & Sons,Inc., (1971), p 454.
6. There is no peak of $[M^+ - \text{  }]$ at all,which indicates the absence of pyridyl ketone group.
7. P. Beak and J. L. Miesel, J. Amer. Chem. Soc., 89, 2375 (1967).
8. J. P. Phillips and F. C. Nachod (Ed.),"Organic Electronic Spectral Data", Interscience Publ., New York, London, Vol III (1958) p 68.
9. R. A. Neunteufel and D. R. Arnold, J. Amer. Chem. Soc., 95, 4080 (1973).
10. H. E. Popkie and J. B. Moffat, Can. J. Chem., 43, 624 (1965).
11. A. H. Cook and D. G. Jones, J. Chem. Soc., 278 (1941).
12. The α-protons of pyridines are shifted to low field, for example,

2-methylpyridine (τ): H_6,1.49; H_5,3.08; H_4,2.57; H_3,3.00. 4-cyanopyridine (τ): H_2,0.95; H_3,2.00. [J. W. Emsley, J. Feeney and L. H. Sutcliffe,"High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergamon Press, (1966), p 795.]

13. Judging from melting points and spectral data, 4 is not a known bipyridine-carbonitrile. The following are known. [3,3'-Bipyridine]-5-carbonitrile (Chem. Abstr., 67, 99969r (1967)). [3,4'-Bipyridine]-3'-carbonitrile (ibid., 67, 82057u (1967)). [2,2'-Bipyridine]-4-carbonitrile and [4,4'-bipyridine]-3-carbonitrile (V. B. Leont'ev, O. S. Otroshchenko, Y. S. Mangutova and A. S. Sadykov, Zh. Obshch. Khim., 35, 297 (1965)). [2,2'-Bipyridine]-5-carbonitrile (Chem. Abstr., 63, 8309d (1965)). [2,3'-Bipyridine]-5-carbonitrile and [2,3'-bipyridine]-5'-carbonitrile (M. Goshaev, O. S. Otroshchenko, V. B. Leont'ev and A. S. Sadykov, Izv. Akad. Nauk Turkm. SSR, Ser. Fiz.-Tekh., Khim. Geol. Nauk, 109 (6) (1971)).

Figure 1. Stern-Volmer plots for fluorescence quenching of 1 by 2-cyanopyridine in acetonitrile.



S U M M A R Y

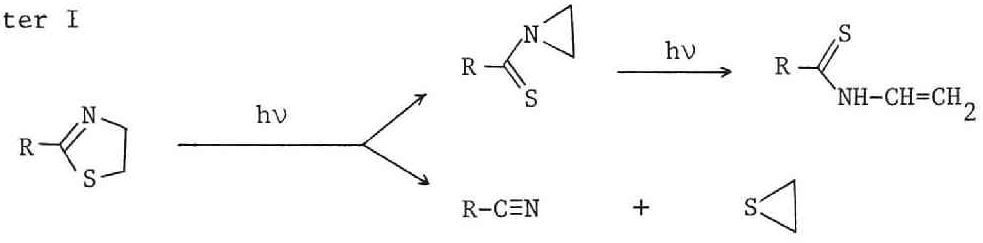
The present volume (Part I) sheds light on general reaction types of five-membered dihydroheteroaromatics caused by light, and they are summarized in General Introduction. In Part II, interesting reactions which are interpreted in terms of exciplex and radical ion formation are presented for imidazole-nitrile systems.

Part I. Chapter I : Upon photolysis, 2-alkyl-2-thiazolines underwent rearrangement to N-alkenylthioamides as the major pathway and fragmentation to a nitrile and an episulphide as the minor one. Evidences are provided for the intermediary formation of a valence bond isomer, N-thioacylaziridine, followed by its photochemical transformation into N-alkenylthioamides. Chapter II : Upon photolysis, 2-isoxazolines undergo three types of formal [2 + 2] reactions in addition to 1,2-bond cleavage followed by further transformation. For example, 3,5-diphenyl-2-isoxazoline gave benzonitrile, 4,5-diphenyl-3-oxazoline, benzaldehyde, styrene, β-aminochalcone and 2-phenylquinoline. 4,5-Diphenyl-3-oxazoline was shown to be formed via fragmentation into 2-phenylazirine and benzaldehyde followed by photochemical recombination, and 2-phenylquinoline via 1,2-bond cleavage followed by recyclization. Chapter III : Two modes of the photochemical cis-trans isomerization of cis- and trans-2,4,5-triphenylimidazolines are presented, that is, pathways via an imidazolinyl radical (in acetone) and via 4,5-bond cleavage (in acetonitrile and

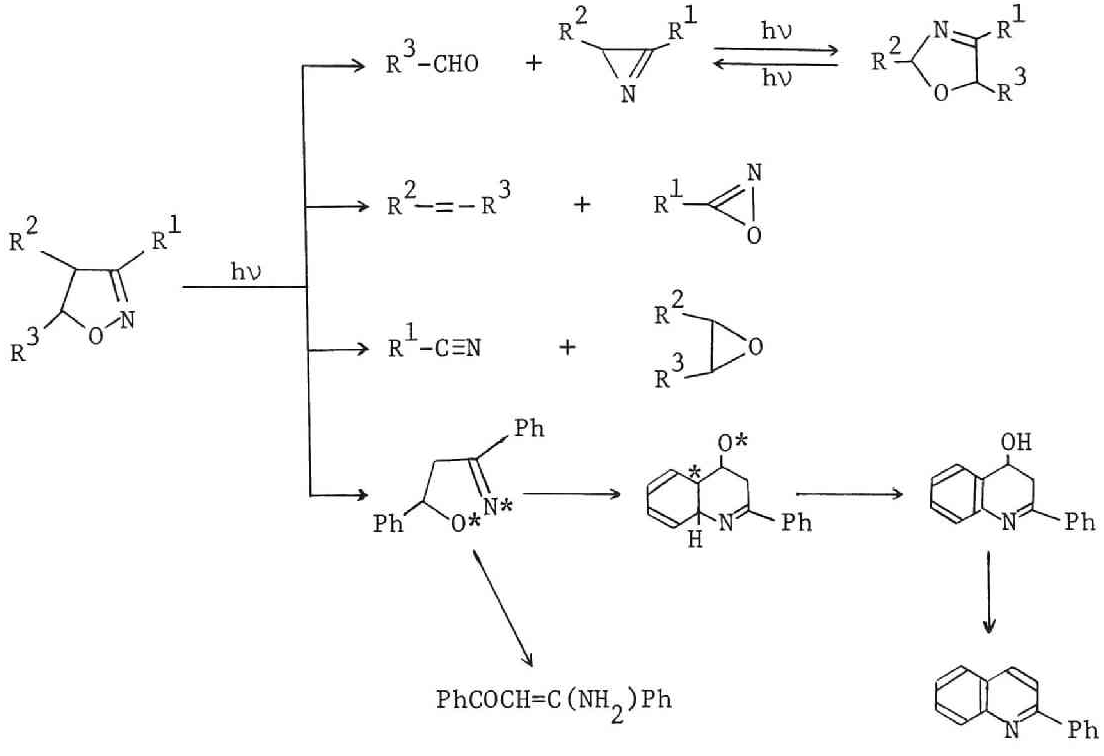
benzene). Chapter IV and V : Imidazolines were found to be dehydrogenated to imidazoles by excited acetone. From various data it is suggested that the imidazolinyl radical reverts to the parent imidazoline by hydrogen transfer from the acetone ketyl radical during the course of photolysis. The photoaromatization with excited acetone was applied to other dihydroaromatic compounds with some success.

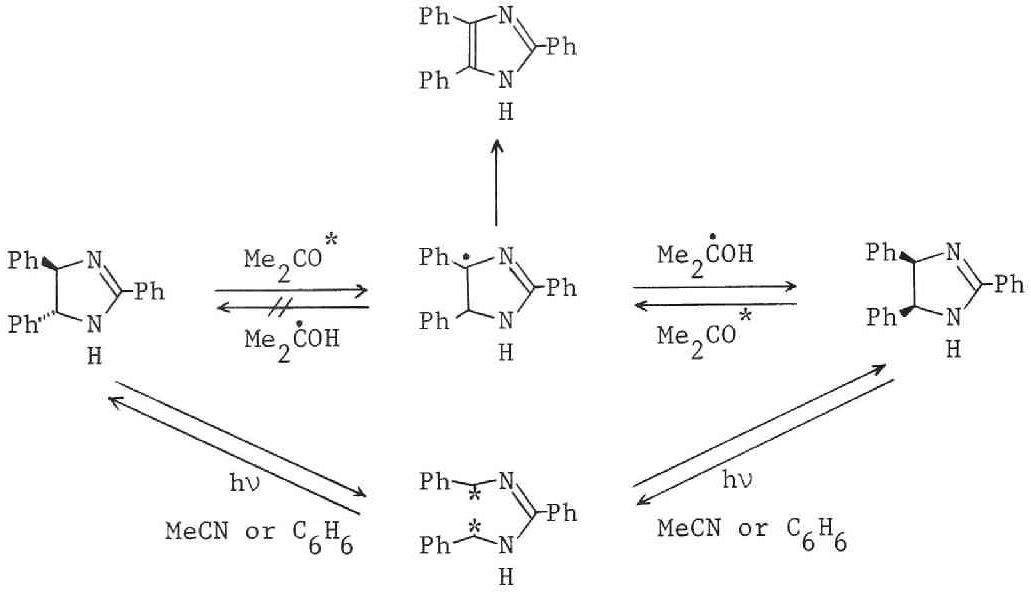
The above reactions are illustrated below.

Chapter I

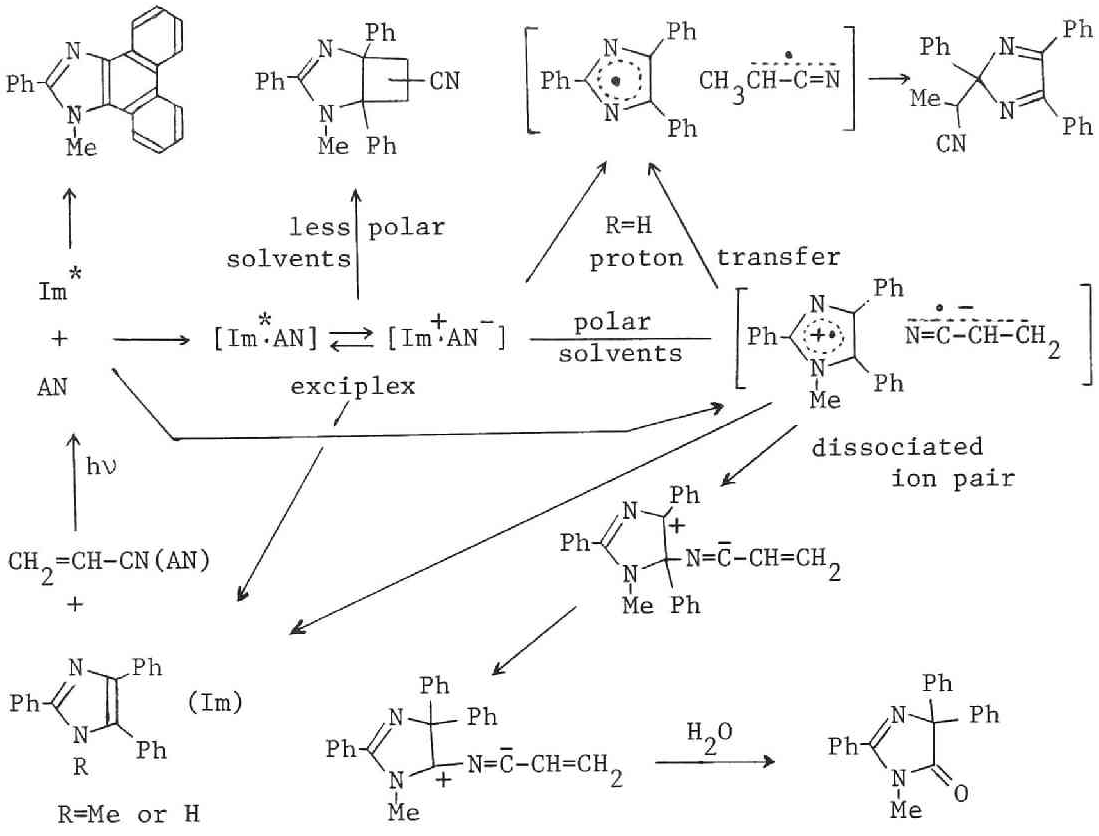


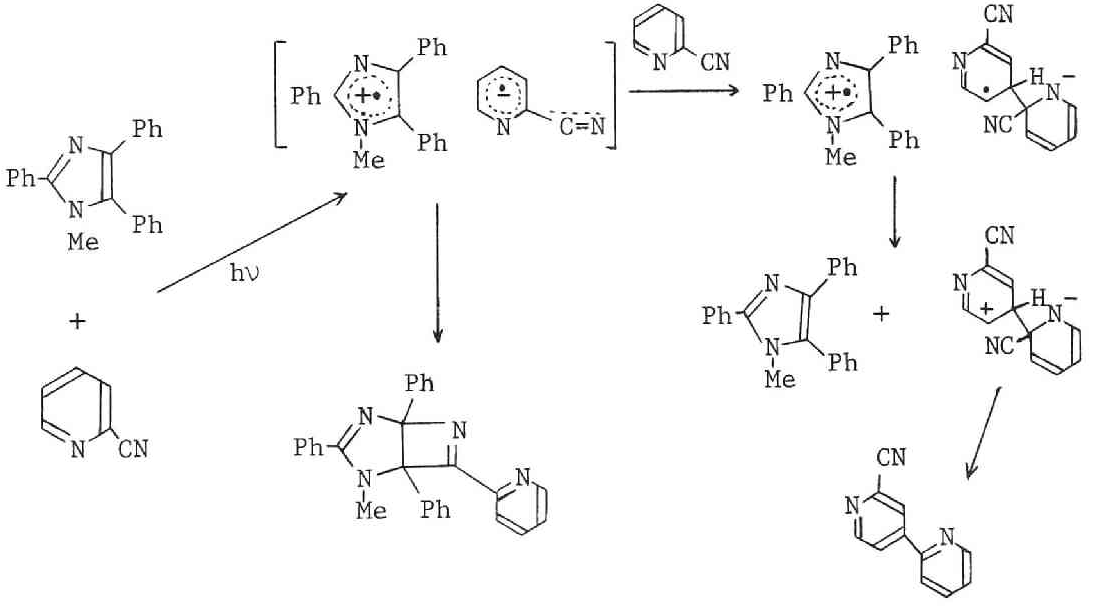
Chapter II





Part II. Acrylonitrile photochemically adds to N-unsubstituted imidazoles resulting in α-cyanoethylation both in ethanol and in acetonitrile. On the other hand, N-substituted imidazoles react photochemically with acrylonitrile either to afford [2 + 2] cycloadducts in solvents having medium or low polarity such as ethanol or to afford Δ^2-imidazolin-5-ones in highly polar solvents such as acetonitrile. Photolysis of N-substituted imidazoles with 2-cyanopyridine afforded a novel cycloadduct between the imidazole and the cyano group in addition to a bipyridine-carbonitrile. These reactions are illustrated below. It is suggested from various data that an exciplex and/or a dissociated ion pair participate in these reactions.


less polar solvents
R=H proton transfer
polar solvents
exciplex
dissociated ion pair
hν
(Im)
R=Me or H
H_2O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LIST OF PUBLICATIONS

PART I

CHAPTER I

T. Matsuura and Y. Ito, J. C. S. Chem. Comm., 897 (1972).

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CHAPTER V

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PART II

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CHAPTER II

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CHAPTER III

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